



AD

AD 741362

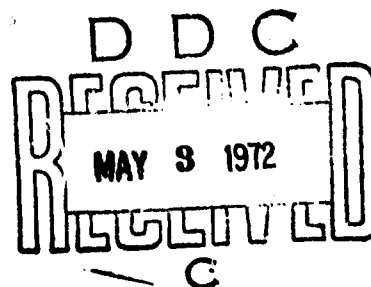
## TECHNICAL REPORT

WVT-7150

RHENIUM ALLOYS - IRON GROUP METALS  
(ELECTRODEPOSITION AND PROPERTIES)

Reproduced by  
NATIONAL TECHNICAL  
INFORMATION SERVICE  
Springfield, Va. 22151

OCTOBER 1971



# BENET R&E LABORATORIES

## WATERVLIET ARSENAL

WATERVLIET-NEW YORK

AMCMS No. 4932.08.87997

APPROVED FOR PUBLIC RELEASE; DISTRIBUTION UNLIMITED

70

## DISPOSITION

Destroy this report when it is no longer needed. Do not return it to the originator.

## DISCLAIMER

The findings in this report are not to be construed as an official Department of the Army position unless so designated by other authorized documents.

ACCESSION FOR	
CFBTI	WHITE SECTION <input checked="" type="checkbox"/>
DDC	BUFF SECTION <input type="checkbox"/>
UNANNOUNCED	<input type="checkbox"/>
JUSTIFICATION .....	
BY .....	
DISTRIBUTION/AVAILABILITY CODES	
DIST.	AVAIL. AND/OR SPECIAL
A	

WVT-7150

RHENIUM ALLOYS - Iron Group Metals (Electrodeposition and Properties)

TECHNICAL REPORT

BY

V. PETER GRECO

OCTOBER 1971

Work performed in fulfillment of requirements for his Master of Science Degree at Rensselaer Polytechnic Institute.

Unclassified  
Security Classification

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author) Watervliet Arsenal Watervliet, N.Y. 12189		2a. REPORT SECURITY CLASSIFICATION Unclassified	
2b. GROUP			
3. REPORT TITLE RHENIUM ALLOYS - Iron Group Metals (Electrodeposition and Properties)			
4. DESCRIPTIVE NOTES (Type of report and inclusive dates) Technical Report			
5. AUTHOR(S) (First name, middle initial, last name) V. Peter Greco			
6. REPORT DATE October 1971		7a. TOTAL NO. OF PAGES 70	7b. NO. OF REFS 57
8a. CONTRACT OR GRANT NO. AMCMS No. 4932.06.67997		8b. ORIGINATOR'S REPORT NUMBER(S) WVT-7150	
8c. PROJECT NO.		8d. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)	
10. DISTRIBUTION STATEMENT Approved for public release; distribution unlimited.			
11. SUPPLEMENTARY NOTES		12. SPONSORING MILITARY ACTIVITY U. S. Army Weapons Command	
13. ABSTRACT The electrodeposition of thick deposits of rhenium co-deposited with the iron group metals (binary systems) from various electrolytes has been investigated. Microstructures of some of the alloys are shown and some of their properties have been evaluated and discussed. The behavior of the alloys (15-45 weight per cent Re) after heat treatment at temperatures ranging from 600-1800°F have been studied and the microstructural and microhardness changes are presented. Crystallography of the Co-Re system before and after heat treatment is also discussed. The effects of inert sub-micron sized dispersoids of $Al_2O_3$ on the microstructure and properties of Co-Re alloy coatings is presented. ( ) Electrodeposits of Co-Re and Fe-Re alloys can be obtained that are sound, thick (3-7 mils) and smooth and which could be considered for industrial applications. The results for the Ni-Re system were less satisfactory. The Co-Re alloys exhibit a significant increase in microhardness after heat treatment at 600°F which does not decrease until heat treating temperature exceeds approximately 1500°F. The microstructures of the alloys are laminar superimposed over a columnar structure. Data showing the increase in hardness and in the recrystallization temperature of cobalt with alloying additions of Re and $Al_2O_3$ dispersoids are also given.			

DD FORM 1473  
1 NOV 65

REPLACES DD FORM 1473, 1 JAN 64, WHICH IS  
OBSOLETE FOR ARMY USE.

Unclassified  
Security Classification

145

**Security Classification**

## TABLE OF CONTENTS

	Page
LIST OF TABLES . . . . .	v
LIST OF FIGURES . . . . .	vi
ACKNOWLEDGEMENT . . . . .	viii
ABSTRACT . . . . .	ix
I. INTRODUCTION . . . . .	1
II. BACKGROUND . . . . .	3
A. Historical . . . . .	3
B. Metallurgical Studies . . . . .	3
C. Electrodeposition Studies . . . . .	4
1. Rhenium . . . . .	4
2. Rhenium Alloys . . . . .	4
D. Properties of Rhenium . . . . .	5
III. OBJECTIVES . . . . .	9
IV. THEORETICAL CONSIDERATIONS . . . . .	10
A. Electrochemical Principles . . . . .	10
B. Theory of Rhenium Electrodeposition . . . . .	13
C. Theory of Rhenium Alloy Electrodeposition . . . . .	13
D. Phase Diagrams of Iron Group Metals Alloyed with Rhenium . . . . .	14
V. EXPERIMENTAL PROCEDURE . . . . .	21
A. Plating Baths . . . . .	21
B. Bath Preparation . . . . .	23
C. Preparation of Electrocomposites of Co-Re with Al <sub>2</sub> O <sub>3</sub> Particles . . . . .	23
D. Electrolysis . . . . .	24
E. Analysis of Deposits . . . . .	24
F. Heat Treatment . . . . .	25
G. Hardness Measurements . . . . .	25
H. Photomicrographs . . . . .	25
I. Xray Analysis . . . . .	26
J. Microprobe Analysis . . . . .	26

	Page
VI. EXPERIMENTAL RESULTS	27
A. Evaluation of Electrolytes . . . . .	27
1. Control of Plating Conditions . . . . .	27
2. Surface Appearance of Alloy Deposits . .	29
3. Weight % Re in Alloy Deposits . . . . .	31
4. Microstructures of Rhenium Alloyed with Iron Group Metals . . . . .	33
5. Observations of Some Growth Habits . . .	36
6. Evaluation of Plating Baths and Alloy Systems . . . . .	40
B. Evaluation of Co-Re Alloys . . . . .	42
1. Relation of Hardness to Heat Treatment of Co-Re Alloys . . . . .	42
2. Effect of Heat Treatment on Micro- structure of Cobalt and Cobalt Rhenium Alloy . . . . .	43
3. Effect of Re Concentration on Hardness. .	46
4. Hardness Band of Co-Re Alloys . . . . .	46
5. Relation of Hardness to Heat Treatment of Dispersion Hardened Co-Re Alloys . . .	48
6. X-ray Examination of Cobalt-Rhenium Alloys . . . . .	51
VII. CONCLUSIONS . . . . .	55
VIII. RECOMMENDATIONS . . . . .	57
IX. LITERATURE CITED . . . . .	58

# LIST OF TABLES

		Page
Table I	Composition of Baths for Codepositing Rhenium with the Iron Group Metals . . . . .	22
Table II	Operating Conditions for Codepositing Rhenium with the Iron Group Metals . . . . .	28
Table III	Results from Preliminary Studies of the Various Baths . . . . .	30
Table IV	Xray Data of Various Co-Re Alloys . . . . .	54



# LIST OF FIGURES

	Page
Figure 1. Equilibrium Diagram of the Nickel - Rhenium System . .	15
Figure 2. Equilibrium Diagram of the Cobalt - Rhenium System . .	17
Figure 3. Equilibrium Diagram of the Iron - Rhenium System . . .	19
Figure 4. Surface View of Crack-Free Electrodeposited Co-Re in Contract to Chromium Revealing Stress Cracks (Original Magnification x 200) . . . . .	32
Figure 5. Relation of Deposit Composition with Bath Concen- tration with Respect to Rhenium in Co-Re Electrodeposits (Bath 6) . . . . .	34
Figure 6. Relation of Deposit Composition with Cathode Current Density Using Bath 3 and 6 . . . . .	35
Figure 7. Microstructures and Properties of Ni-Re Alloys Electrodeposited under Various Plating Conditions (Cross-Sectioned Perpendicular to Base Metal) . . . . .	37
Figure 8. Microstructures and Properties of Ni-Re Alloys Electrodeposited under Various Plating Conditions (Cross-Sectioned Perpendicular to Base Metal) . . . . .	38
Figure 9. Microstructures and Properties of Co-Re and Fe-Re Alloys Electrodeposited under Various Plating Conditions (Cross-Sectioned Perpendicular to Base Metal) . . . . .	39
Figure 10. Some Growth Habits of Cross Sectioned Co-Re Electro- deposited Alloys from Bath 6 ..... (Orig. Mag. x500)	41
Figure 11. Relation of Room Temperature Microhardness to Heat Treatment of Electrodeposited Cobalt and Cobalt- Rhenium Alloys (Bath 6) . . . . .	44
Figure 12. Effect of Heat Treatment (in Hydrogen Atmosphere) on the Microstructures of Electrodeposited Cobalt and Cobalt-Rhenium Alloy (28.74 wt. % Re) from Bath 6. Cross-Sectioned Perpendicular to Base Metal (Original Magnification x500) . . . . .	45
Figure 13. Relation of Room Temperature Microhardness to Wt % Re in Cobalt Alloy Deposits for Two Heat Treatments and Two Atmospheres (Combined Data from Baths 6 and 7)	47

	Page
Figure 14. Microhardness Band of Co-Re Alloys vs Post Heat Treatment (Combined Data from Baths 6 and 7) .	49
Figure 15. Microstructures of Various Co-Re Alloys (Bath 6) before and after Post Heat Treatment at 1800°F. (Cross-Sectioned Perpendicular to Base Metal)... (Original Magnification x500) . . . . .	50
Figure 16. Relation of Room Temperature Microhardness to Heat Treatment for a Co-Re ( $Al_{2/3}O_3$ ) Alloy (Bath 6) . . .	52

#### ACKNOWLEDGEMENT

The author wishes to express his gratitude to Professor P.J. Diefendorf for the direction and guidance received from him for conducting the study and preparing the thesis. Special thanks are extended to William Baldauf for his assistance in conducting many of the plating experiments; to Mrs. T. Brassard for her efforts in preparing the photomicrographs and to George Capsimalis for the X-ray diffraction measurements.

Finally, the author is especially grateful to Mrs. P. Exner and to Miss Clare Szymanski for the preparation and proofreading of the typed manuscript.

## ABSTRACT

The electrodeposition of thick deposits of rhenium co-deposited with the iron group metals (binary systems) from various electrolytes has been investigated. Microstructures of some of the alloys are shown and some of their properties have been evaluated and discussed. The behavior of the alloys (15-45 weight per cent Re) after heat treatment at temperatures ranging from 600-1800°F have been studied and the microstructural and microhardness changes are presented. Crystallography of the Co-Re system before and after heat treatment is also discussed. The effects of inert sub-micron sized dispersoids of  $Al_2O_3$  on the microstructure and properties of Co-Re alloy coatings is presented.

Electrodeposits of Co-Re and Fe-Re alloys can be obtained that are sound, thick (3-7 mils) and smooth and which could be considered for industrial applications. The results for the Ni-Re system were less satisfactory. The Co-Re alloys exhibit a significant increase in microhardness after heat treatment at 600°F which does not decrease until heat treating temperature exceeds approximately 1500°F. The microstructures of the alloys are laminar superimposed over a columnar structure. Data showing the increase in hardness and in the recrystallization temperature of cobalt with alloying additions of Re and  $Al_2O_3$  dispersoids are also given.

## PART I

## INTRODUCTION

Numerous claims are reported in the literature on the electro-deposition of refractory metals in the pure state in aqueous electrolytes. The original claims and failures of investigators to reproduce the results with metals such as tungsten or molybdenum have been reported in a number of publications and patents which have been reviewed by Blum & Hogaboom<sup>1</sup>, Lowenheim<sup>2</sup>, and more recently evaluated in an excellent treatise by Brenner<sup>3</sup>. The evidence indicates that rhenium is the only refractory metal which can be electrodeposited.

The properties of rhenium have been the subject of increasing interest in recent years. Some of the more important properties of rhenium deposits which are responsible for its commercial success are its high melting point and high values of chemical resistance, hardness, and wear resistance. However, electrodeposited rhenium has some shortcomings which have limited its use to a minimum of industrial applications. For example: 1. The cathode current efficiency of rhenium in aqueous solutions is low. 2. Deposits which exceed approx. 2 microns are generally cracked due to residual stresses. 3. Rhenium is known to have relatively poor oxidation resistance. Far more important than the above limitations is the high cost (similar to platinum) which has kept rhenium from being a valuable engineering material. Most of the above shortcomings can be circumvented, however, by codepositing rhenium with the iron group metals. In this manner the current efficiency is increased, stress cracks are minimized or

eliminated, mechanical and chemical properties are improved, thickness can be increased and most important of all will be the consumption of less rhenium. Furthermore, rhenium and its alloys possess many other valuable properties, although many of these have only been studied with the thermally prepared forms of the metal and its alloys.

While as-deposited alloys are not normally in thermodynamic equilibrium, it has been well established by X-ray diffraction data that they are true alloys and can form crystal types which are the same as predicted by the phase diagram determined from thermally prepared alloys<sup>4</sup>.

The remarkable difference between electrocrystallized alloys and those from the melt are the presence of solid solutions of simultaneously discharged metals whether or not the phase diagram shows the solid solution phase<sup>4</sup>. For example, according to the phase diagram lead is essentially insoluble in copper but electrolytically prepared copper-lead deposits have been found to be solid solution type alloys which are metastable. Another important difference is that the hardness, grain size and microstructure of electrocrystallized alloys can be altered considerably by varying plating conditions in addition to heat treatment. Therefore, electro-deposited alloys can perform in a superior manner in many commercial applications such as electrolytically prepared brass, bronze, Pb-Sn, Ni-Co as well as others. A reasonable expectation, therefore, is that not only should some of the alloying effects of rhenium found in thermally prepared alloys be imparted to electrolytically prepared alloys after suitable heat treatment but improved alloys may be obtained.

This thesis will deal with some of the metallurgical properties of rhenium alloyed with the iron group metals by electrodeposition. A brief review of rhenium from its origin to this present day is given below which includes other properties, alloying effects and successful applications.

## PART II

### BACKGROUND

#### A. HISTORICAL

Credit for the discovery of rhenium (in 1925) was given to Noddack, Tacke and Berg of Germany, who first isolated and concentrated the pure metal which was given the name rhenium (Rhinemetal) after the river Rhine. Shortly after its discovery, rhenium received little commercial attention because of its being widely scattered in the earth's surface in small concentrations which resulted in high cost. However, during the past two decades, rhenium has gained significant recognition as a high performance engineering material prepared either thermally (e.g., arc cast or sintering) as a metal or alloy or in a few cases electrolytically as a metal.

#### B. METALLURGICAL STUDIES

An excellent survey combined with further investigations on the fabrication and forming of rhenium and its alloys has been conducted by Sims et al<sup>5,6,7</sup> under the sponsorship of an Air Force contract. In recognizing the potential of the metal, the Electrochemical Society (in 1960) held a symposium on rhenium<sup>8</sup>. At this symposium,

comprehensive coverage was given to the physical metallurgy and properties of the metal and its alloys which have led to some successful industrial applications. More recent data on the significant alloying effects of rhenium on tungsten and molybdenum and their applications have been presented by Port<sup>9</sup>.

## C. ELECTRODEPOSITION STUDIES



### 1. RHENIUM

Rhenium electrodeposition was first reported by Fink and Deren<sup>10,11</sup> in 1934 from a number of aqueous plating baths. Following their work, a number of publications and patents on the electrodeposition of rhenium were added to the literature by other investigators<sup>12-20</sup>.

A well documented characteristic behavior of the shiny as-plated rhenium found in the cited literature is its unstableness in moisture (turning dark in color). Heat treatment at 950-1000°C in hydrogen (15-60 min.) is required to impart tarnish-resistance to the metal. A proposed explanation<sup>20</sup> is that rhenium is deposited as rhenium hydride which is decomposed to metal and hydrogen during firing at 950°C. Camp<sup>18</sup> reported that the darkening of rhenium can also be overcome by plating in a proprietary slightly acid phosphate bath at a lower cathode efficiency, thus avoiding the heating in hydrogen.

### 2. RHENIUM ALLOYS

The work performed by Fink and Deren also stimulated the efforts of Netherton and Holt<sup>21,22</sup> whereby they prepared ammoniacal citrate baths for the electrodeposition of binary alloys of rhenium with the iron group metals. Their work involved the study of effects



Reproduced from  
best available copy.



of bath composition and plating conditions on cathode efficiency and on the composition of relatively thin alloy deposits. These alloy deposits were found to be highly resistant to the darkening which pure rhenium deposits experienced when exposed to air for a long time. The latter work was further explored with Ni-Re by Sominskaya et al as reported by Savitskiy, et al<sup>23</sup>.

Korovin and Ronzhin<sup>24</sup> co-deposited high percentages of Re with Nickel using ammonium sulphate to improve the buffering capacity of the electrolyte. Their results showed that alloy composition was determined by the Ni: (Ni+Re) ratio in solution and depended little on current density, temperature or pH of the electrolyte. Savitskiy et al<sup>23</sup> reported that more recent studies by Sominskaya and Nikitina produced sound Re-Ni deposits up to 30 microns (approx. 1 mil).

Phenium-chromium binary coatings were reported by Kvokova and Lainer<sup>16</sup> in studies of thick, dense coatings.

#### D. PROPERTIES OF RHENIUM

The physical and mechanical properties of rhenium is considerably scattered in the various literature previously cited. However, a consolidated review of many of these properties can be obtained in a paper by Sims, et al<sup>25</sup>. Some of the more attractive properties which illustrate rhenium's potential as an engineering material are as follows:

Phenium is hexagonal close-packed (HCP) in structure; has a high melting point (3167°C), and density (21.04 g/cc), is relatively hard

(i.e., electrolytically 494 Vickers compared to 525 for Cr) and has high wear resistance and a low coefficient of friction. Rhenium work-hardens more than any other known pure metal, but on annealing, becomes quite soft and ductile. The metal has a low vapor pressure, outstanding resistance to the "water cycle effect" \* and does not form stable hydrides, carbides or nitrides<sup>26</sup>.

The metal has high strength (160 Ksi T.S. in the annealed condition for 10 mil sheet or 1/8" rod)<sup>27</sup> and retains its strength at high temperature (e.g., 80 Ksi T.S. at 1100°F). It has been well established that unlike molybdenum or tungsten, rhenium does not go through a ductile-to-brittle transition<sup>26</sup> (even in the recrystallized condition).

Its distinctive property among the refractory metals is its high ductility, retention of ductility after thermal cycling (unlike tungsten) and its ductilizing effect when alloyed with other refractory metals (e.g., tungsten and molybdenum). It has also been established that adding as little as 2% rhenium to nickel shifts the temperature at which recrystallization starts from 400°C to 600°C<sup>28</sup>.

The electrical resistivity of the metal is about 4 times that of tungsten (19.14 vs 5.5 microhm-cm at 20°C). Rhenium has shown

---

\*Electrical or electronic filaments in vacuum or inert gas tubes are exposed to unavoidable residual water vapor. Therefore in the presence of water vapor, detrimental reactions occur with metals such as tungsten which results in transfer of metal from the filament to envelope walls. Rhenium and Re-W alloy is resistant to this effect.

high erosion resistance as an electrical contact material in high current cycling in both air atmosphere and submerged in oil<sup>29</sup>. The lower oxides of rhenium are semiconductive<sup>30</sup> which offers high reliability in electrical contacts.

The best established uses for rhenium and rhenium alloys to date are in the lamp and electronics field. For example tungsten-rhenium (W-3% Re) alloys are used for heated cathodes and power tubes. Also 1-10% rhenium in nickel improves the high temperature mechanical properties of thermionic cathodes<sup>31</sup>.

Rhenium is unattacked by hydrochloric acid, resistant to sulfuric acid but dissolves readily in nitric acid. It is highly resistant to attack by molten tin, silver, copper and aluminum. A rather thorough quantitative study on the corrosion and electrochemical behavior of rhenium in various media was conducted by Tamashov and Matveeva<sup>32</sup>.

Rhenium and its compounds, corresponding to all of the oxidation states from -1 to +7\*, have been extensively treated in a monograph by Druce<sup>33</sup>. The most common of its oxides is rhenium heptoxide,  $\text{Re}_2\text{O}_7$ , which is readily formed by exposure of the metal to moist air, or by heating and the oxide is highly volatile. The melting point of  $\text{Re}_2\text{O}_7$  is 297°C and it can be reduced by hydrogen,

---

\*According to Pauling<sup>34</sup> this is the only known occurrence of a metal with a negative oxidation number.

CO, SO<sub>2</sub> and other reducing agents to lower oxides or the pure metal. The oxide Re<sub>2</sub>O<sub>7</sub> is readily soluble in water, hydrolyzing to form the strong acid, HReO<sub>4</sub>.

In the case of hot working of the metal, rhenium appears to be characterized by hot shortness<sup>26</sup>. The hot shortness is reported to be caused by the low melting Re<sub>2</sub>O<sub>7</sub>, which readily forms at grain boundaries when rhenium is hot worked in air. It appears that unless rhenium is alloyed, the metal must be protected by other coatings, or reducing or inert atmospheres in order to utilize its high temperature strength capabilities.

The favorable wear and frictional properties of rhenium coatings were reported by Rabinowicz<sup>35</sup> and more recently by DePew and Larsen<sup>36</sup>. Buckley & Johnson<sup>37</sup> have shown that for low friction and low wear, a metal should have not only a hexagonal crystal structure, but a high ratio of c to a dimension in its crystal lattice. Thus cobalt, with a c/a ratio of 1.625, results in low friction and Rabinowicz<sup>35</sup> shows rhenium, with a c/a ratio of 1.615, to also result in low friction. The wear and frictional behavior of silver-rhenium alloy coatings were reported by Turns<sup>38</sup>.

Root and Beach<sup>39</sup> successfully demonstrated the ductilizing effect of rhenium by first plating rhenium on a tungsten wire (for filaments) and then heating to attain diffusion. The resulting wire was found to be very ductile in bend tests while an uncoated tungsten wire was

generally brittle. In their electrodeposition studies, Netherton and Holt<sup>21</sup> observed that rhenium-nickel alloys were less effected than rhenium when-exposed to air, water, acids and bases.

### PART III

#### OBJECTIVES

In summarizing the general properties of rhenium metal one may conclude that the greatest benefits which may be derived from the use of the metal is by utilizing its alloying effects on other metals to tailor their properties for high performance applications. However the metallurgical properties of coatings of rhenium when codenosed with the iron group metals have not been studied and the deposition of relatively thick ( $>1$  mil) rhenium alloy deposits have not been reported. As previously discussed, studies of electrodeposited rhenium alloys have been directed to the concentration of the bath and process controls and their effects on the composition of the deposits produced which were relatively thin ( $<1$  mil).

The purpose of this present study was to:

1. Explore the plating conditions to produce sound and relatively thick (3 to 7 mils) deposits of various compositions of rhenium codenosed with the iron group metals with emphasis given to cobalt.
2. To evaluate some of the metallurgical properties and microstructures of the alloy coatings after post heat treating in the range  $600^{\circ} - 1800^{\circ}\text{F}$ .

3. To determine the effects of inert sub-micron sized dispersoids of  $Al_2O_3$  on the microstructures and properties of Co-Ra alloy coatings.

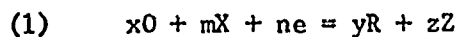
#### PART IV

#### THEORETICAL CONSIDERATIONS

##### A. ELECTROCHEMICAL PRINCIPLES

The fundamentals of alloy deposition have been presented by a number of authors, among which are Brenner<sup>40</sup>, Raub and Muller<sup>4</sup>, and Faust<sup>41</sup>. The same principles and control variables apply to alloy deposition as to single-metal deposition but the problems which evolve in codeposition become more complex. In order to codeposit two or more metals, the variables must be combined in a way that causes the metals to codeposit at the same potential<sup>41</sup>. The deposition potential of a metal or alloy is determined by the activities of cations and anions in the cathode "film" and by the temperature. The activities are functions of the ion concentrations which, in the cathode film, are determined by the rates of deposition, by the ion concentration in the bath, and by the rates of diffusion of the ions involved.

An oxidation-reduction reaction can be represented<sup>42</sup> by the following general equation:



in which "O" and "R" represent the two components of the oxidation-reduction couples; X and Z are substances involved in the process

(which in many chemical equilibria are hydrogen ion and water); and  $x$ ,  $m$ ,  $n$ ,  $y$  and  $z$  are stoichiometric coefficients.

To determine the potential " $E$ " of a system in which the reactants are not at unit activity, the familiar Nernst equation which corresponds to reaction (1) has been employed:

$$(2) \quad E = E^{\circ} + \frac{RT}{nF} \ln \frac{a_{\text{oxid}}}{a_{\text{red.}}}$$

$n$  = # of electrons transferred

$a_{\text{oxid}}$  = activities of oxidized species

$a_{\text{red.}}$  = activities of reduced species

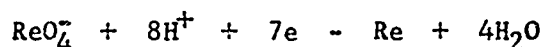
or

$$(3) \quad E = E^{\circ} + \frac{RT}{nF} \ln \frac{a_{\text{O}}^x a_{\text{X}}^m}{a_{\text{R}}^y a_{\text{Z}}^z}$$

in which the  $a$ 's are the activities of the substances involved,  $R$  is the gas constant,  $T$  the absolute temperature, and  $F$  the faraday constant.  $E^{\circ}$  is the normal or standard potential for the redox couple being considered.

If the  $E^{\circ}$  values for the two metals to be plated are far apart in the standard emf series then codeposition prospects would appear to be remote. This difference in potential can be eliminated or even reversed by changing the values of the activities of the depositing cation in the film of the electrolyte at the cathode surface. The change in activities can be accomplished by a large change in the concentration of the ions of the depositing metals, such as by complex ion formation.

The discharge potential of rhenium depends on the hydrogen ion concentration<sup>24</sup>. Therefore, the reaction for rhenium electrodeposition in acid media has been expressed as:



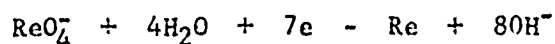
in which the reaction occurs via an intermediate stage. From equation (3), the potential of this reaction is given by the equation

$$(4) \quad E_{\text{Re}} = E_{\text{Re}}^0 + \frac{RT}{7F} \ln a_{\text{ReO}_4^-} \cdot a_{\text{H}^+}^8$$

According to Latimer<sup>43</sup>, the standard potential of Re in acid media is:

$$E_{\text{Re}}^0 = 0.363 \text{ volt}$$

Similarly, in the case of alkaline media, the reaction for rhenium electrodeposition can be expressed as:



The potential of this reaction is given by:

$$(5) \quad E_{\text{Re}} = E_{\text{Re}}^0 + \frac{RT}{7F} \ln \frac{a_{\text{ReO}_4^-}}{a_{\text{OH}^-}^8}$$

The standard potential of Re in alkaline media<sup>43</sup> is:

$$E_{\text{Re}}^0 = -0.584 \text{ volt}$$

The Nernst relation, presented above, has been quoted in many texts as a basic principle of alloy plating. However, it is applicable only in cases in which both metals of an alloy are depositing near their equilibrium potentials. Unfortunately, very few alloy plating systems satisfy this condition and the use of the



Nernst equation often has led to incorrect notions concerning alloy deposition<sup>44</sup>. While the equilibrium electrode potentials of the individual metals may be several hundred millivolts apart, alloy deposition occurs in many cases.

In view of the above, theoretical principles have not been very fruitful in the study and development of new alloy plating processes. Therefore, the establishing of suitable types of complexes and bath composition which yield sound alloy deposits can only continue to be done by experimental research.

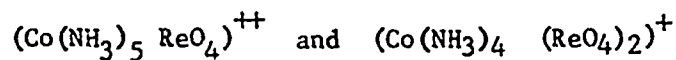
#### B. THEORY OF RHENIUM ELECTRODEPOSITION

Nikežina and Sominskaya<sup>19</sup> investigated the mechanism of rhenium electrodeposition and found that the cathodic current efficiency depended on the state of the electrode surface and that the state of the electrode surface depended on the additives present in the electrolyte. Their studies indicated that ammonium sulfate added to the electrolyte activated the cathode surface.

#### C. THEORY OF RHENIUM ALLOY ELECTRODEPOSITION

According to Netherton and Holt<sup>22</sup>, the mechanism of the cathode process involved in the electrodeposition of rhenium alloys reported by them is somewhat uncertain but they presented the following: The assumed presence of certain types of coordination complexes could explain the alloys with high rhenium content. The formula for one of the cobalt ammine complex rhenium salts that has been previously prepared is  $\text{Co}(\text{NH}_3)_6(\text{ReO}_4)_3$ . According to Werner's theory of

coordination compounds this type of compound may undergo isomerism in solution to give types of ions as follows:

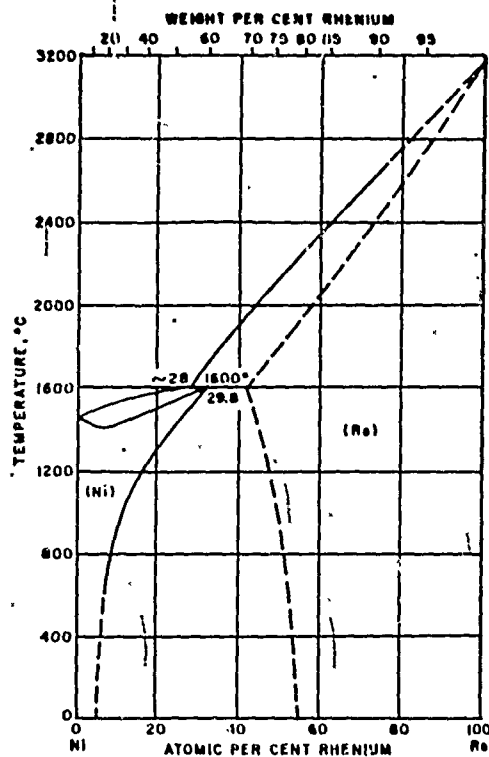


The positive charged complex ions would be transported to the cathode more readily than a negative ion which would approach the cathode by diffusion. It is speculated that the citrate ion in the bath affects the types of complex ions present and thus adds to the complexity of the reduction process. It is evident from the above that the mechanism of the electrodeposition of rhenium alloyed with iron, nickel, and cobalt will not be understood until the electrodeposition of the single metals (Ni, Co, or Fe) from citrate solutions has been studied more extensively.

#### D. PHASE DIAGRAMS OF IRON GROUP METALS ALLOYED WITH RHENIUM

Property benefits can be realized from each of the three alloy systems considered in this study in which the major one is to increase the melting point of iron group metals and still hopefully retain a marginal degree of their ductility. An interesting part of this study is that each of the iron group metals has a different crystal structure which dissolves with HCP rhenium to form single phase solid solution strengthened alloys for the concentrations studied in this investigation.

Ni-Re      The diagram in figure 1 is the work of Pogodin and Skryabina (1) (see figure 1) as presented by Elliot<sup>45</sup>, who determined the equilibrium by thermal, metallographic, and X-ray analysis of alloys prepared



[1] S. A. Pogodin and M. A. Skryabina, *Izv. Sektora Fiz.-Khim. Analiza, Inst. Obshch. i Neorgan. Khim., Akad. Nauk SSSR*, 25, 1954, 81-88.

Figure 1. Equilibrium Diagram of the Nickel - Rhenium System

from high purity Ni and 99.6 - 99.8% Re. There is extensive mutual solubility of the elements with no components existing. The solubility of Re in Ni decreases rapidly with decreasing temperature, whereas the solubility of Ni in Re varies less with temperature. Eliot reported that the minimum in the solidus of Ni is obviously inconsistent with the liquidus since there is no tangency. Since [1] gives data for both liquidus and solidus, it is impossible to judge which is in error.

Reproduced from  
best available copy.

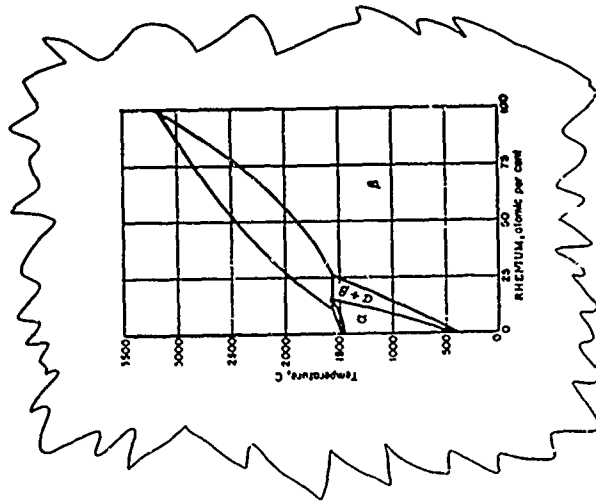


Co-Re

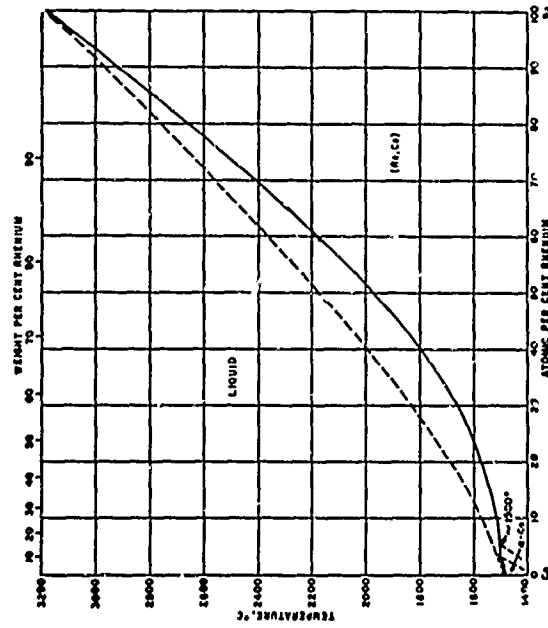
The diagram in figure 2 was presented by Eliot<sup>16</sup> who modified the work of Savitskii and Tylkina [2] to indicate the peritectic formation of  $\alpha$ -Co as predicted by Hansen<sup>47</sup>. The solidus temperature of seven alloys over the whole range of compositions was originally determined by Savitskii and Tylkina [2] who, according to Eliot, erroneously indicated solubility between Re (HCP) and the high temperature allotrope of Co (FCC). The flat portion of the solidus curve observed by Savitskii and Tylkina [2] at the Co-rich end is consistent with such an interpretation. (The inset will be discussed later)

Fe-Re

This system is the most extensively studied of the three binary systems. The phase diagram of the partial system Fe-Re<sub>2</sub>Fe<sub>3</sub> (68.98 wt. % Re) presented



After Koster and Horn



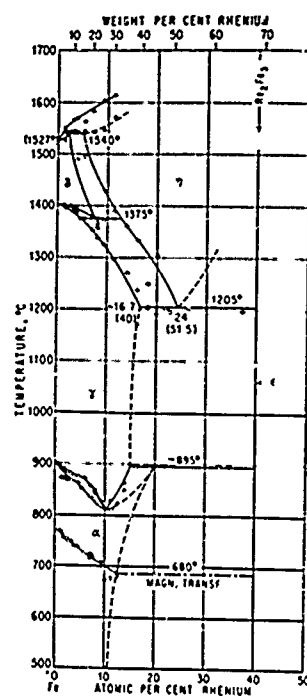
[2] E. M. Savitskiy and M. A. Tytkina, *Zh. Neorgan. Khim.*, 3, 1958, 820-837.

Figure 2. Equilibrium Diagram of the Cobalt - Rhenium System

by Hansen<sup>48</sup> in figure 3 is based on thermal analysis and microscopic data by Eggers (3). X-ray powder patterns, obtained by exposure samples at high temperatures, corroborate the existence of the phases shown. Although the diagram cannot be regarded as representing equilibrium conditions, at least it outlines the phase relationships shown. The five phases found by Eggers (3) in establishing the equilibrium diagram up to 50% rhenium are:

1.  $\epsilon$  -phase - This is probably  $\text{Fe}_3\text{Re}_2$  according to Sims et al<sup>49</sup> and showed a low solubility for iron down to room temperature. It was very hard.
2.  $\eta$  -phase - A phase of wide solubility, apparently based on  $\text{Fe}_3\text{Re}$ , formed at  $1205^\circ\text{C}$ .
3.  $\delta$  -iron - Decomposes eutectoidally to  $\gamma$  - and  $\eta$  -phases at  $1540^\circ\text{C}$ .
4.  $\gamma$  -iron - Face-centered gamma iron which dissolves up to 40% rhenium at  $1205^\circ\text{C}$ .
5.  $\alpha$  -iron - Body-centered alpha which dissolves up to 29% rhenium.

From the standpoint of melting point and ductility, Fe-Re should be the best candidate since iron has a higher M.P. and is BCC in structure. However, iron is allotropic and phase transformations take place at elevated temperatures which must be taken into consideration when rapid



[3] H. Eggers, *Mitt. Kaiser-Wilhelm-Inst. Eisenforsch. Düsseldorf*, 20, 1938, 147-152.

Figure 3. Equilibrium Diagram of the Iron - Rhenium System

changes in temperature take place during service. In addition, compound formation which exists in the Fe-Re system may be detrimental due to brittleness; therefore such concentrations of Re should be avoided.

Reproduced from  
best available copy.



From the standpoint of alloying during co-deposition of two metals, metals with the same crystal structure should alloy easier and produce more homogeneous alloys than two metals with different structures. Therefore Co-Re would meet these requirements and the phase diagram shows a continuous increase in M.P. with increasing Re which is desirable. However, cobalt is also allotropic and unfortunately HCP structures would be expected to be more brittle than cubic structures.

The Ni-Re system is of interest because of the extensive mutual solubility; absence of compound formation; no phase transformations and from a metallurgical standpoint should be less brittle than Co-Re since Ni is FCC in structure.

The above evaluation for the three alloy systems is primarily based on the metallurgists' viewpoint in forming thermal alloys which should also take atomic radii differences into consideration. From this standpoint one may consider the selection of an alloy system without experimentation. However, the success of forming alloys by co-deposition which are sound and which meet the property requirements must also depend on other factors which are based on electrochemical factors. The above metallurgical considerations can only be



considered as a guide and the selection of such alloys by co-deposition for engineering applications must be determined by experimentation and process development.

## PART V

### EXPERIMENTAL PROCEDURE

#### A. PLATING BATHS

The aqueous plating baths investigated (see Table I) were;

1. Nickel plating baths modified by the addition of potassium perrhenate ( $KReO_4$ ). (Bath Numbers 1 and 2)

2. An ammoniacal citrate bath containing  $KReO_4$  or ammonium perrhenate ( $NH_4ReO_4$ ) and nickel, cobalt or iron sulphate. (Bath Numbers 3, 6 and 8)

3. Ammonium sulphate and nickel sulphate with additions of  $KReO_4$ . (Bath Number 5)

4. The last bath studied which has not been previously reported in the literature is the conventional nickel sulfamate bath with additions of  $KReO_4$  or  $NH_4ReO_4$ . (Bath Numbers 4 and 7)

Bath Numbers 4 and 7 were explored because of the relatively low stressed deposits of iron group metals which have been produced in a sulfamate electrolyte. Experiments with Bath 5 follows the work of Korovin and Ronzhin<sup>15</sup>, whereby they reported that the use of ammonium sulphate improved the buffering capacity of the electrolyte in contrast to citric acid.

TABLE I. COMPOSITION OF BATHS FOR CODEPOSITING RHENIUM WITH THE IRON GROUP METALS

Bath No.	Alloy	Bath Formula	Comp'd Conc. g/l	As-Metal Conc. g/l	Metal %Re In Bath	Reference
1	Ni-Re	Nickel Sulfate ( $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ ) Nickel Chloride ( $\text{NiCl}_2 \cdot \text{H}_2\text{O}$ ) Boric Acid ( $\text{H}_3\text{BO}_3$ ) Potassium perrhenate ( $\text{KReO}_4$ )	225 45 30 1	61  0.64	1	(21)
2	Ni-Re	Same as bath (1) plus citric acid [ $\text{C}_3\text{H}_4(\text{OH})(\text{COOH})_3 \cdot \text{H}_2\text{O}$ ]	70			(21)
3	Ni-Re	Nickel Sulfate Citric Acid Potassium perrhenate Ammonium Hydroxide ( $\text{NH}_3\text{OH}$ )	56 66 4 as required	12.5  2.56	17	(21)
4	Ni-Re	Nickel Sulfamate [ $\text{Ni}(\text{NH}_2\text{SO}_3)_2$ ] *Nickel Bromide Concentrate Boric Acid ( $\text{H}_3\text{BO}_3$ ) **Wetting Agent Potassium perrhenate	323 51.2 23.9 0.5 1	75  0.64	0.24	present paper
5	Ni-Re	Nickel Sulfate Ammonium Sulfate [ $(\text{NH}_4)_2\text{SO}_4$ ] Potassium perrhenate	5 50 4	1.1  2.56	70	(24)
6	Co-Re	Cobalt Sulfate ( $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ ) Citric Acid Potassium perrhenate Ammonium perrhenate ( $\text{NH}_4\text{ReO}_4$ ) for Replenisher	60 66 1-30	12.5  0.64-19.2	4.87-60.5	(22)
7	Co-Re	Same as bath (4) except cobalt in place of nickel. Potassium perrhenate	1-4	0.64-2.56	0.84-3.3	present paper
8	Fe-Re	Ferrous Sulfate ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ) Citric Acid Potassium perrhenate Ammonium perrhenate for Replenisher	59.4 6.6 10	12  6.4	35	(22)

\* Supplied by Harstan Chemical Co., N.Y., N.Y.

\*\* "DuPont Me Dry" supplied by DuPont Co.

## B. BATH PREPARATION

All bath constituents (C.P. or reagent grade), except  $\text{KReO}_4$ , were added to distilled water to give a bath of the desired composition. Since  $\text{KReO}_4$  is not very soluble in cold water, it was dissolved in a volume of 250-500ml of the above solution using a hot-water bath. Bath pH was determined by a glass electrode at the operating temperature of the bath and was adjusted with ammonium hydroxide, except for the sulfamate bath which was adjusted with sulfamic acid. Since consumable anodes of cobalt, iron, or nickel were used and periodic additions of rhenium were made during plating, the baths were successfully reused for several platings after correcting the pH for each run. The preliminary experiments of shorter plating cycles were performed without Re replenishment, in order to attempt to duplicate the results of other investigators.

Reproduced from  
best available copy.



For the earlier platings, potassium perrhenate was first used in the initial bath make-up and as the replenisher. However, during the later experiments, ammonium perrhenate became available and was preferable as the replenisher. The solubility of  $\text{NH}_4\text{ReO}_4$  is much greater than  $\text{KReO}_4$  and most useful in baths operated at lower temperatures (such as the sulfamate bath). The percent of rhenium metal in  $\text{KReO}_4$  is 64.3% as compared to 69.4% for  $\text{NH}_4\text{ReO}_4$ .

## C. PREPARATION OF ELECTROCOMPOSITES OF Co-Re WITH $\text{Al}_2\text{O}_3$ PARTICLES

The preparation of dispersion strengthened alloys by electro-deposition had originally been reported by Sautter<sup>50</sup>, and later by Browning et al<sup>51</sup>, Greco and Baldauf<sup>52</sup> and others and, therefore, will

not be discussed in this writing. Submicron ( $0.05\mu$ )  $Al_2O_3$  particles were mixed in the electrolyte at concentrations of 50 g/l. Agitation of the electrolyte during electrodeposition was sufficient to maintain the particles in suspension. This permitted the particles to collide on the cathode surface during deposition and subsequently entrap themselves in the matrix of the Co-Re alloy.

#### D. ELECTROLYSIS

Direct current was supplied by a R.O. Hull model selenium type rectifier with a variable voltage control. The immersed portion of the anodes employed were approximately  $3/4$  in. x 2 in. in dimension. The cathodes were copper, stainless steel (300 series) or carbon steel with the effective plating area measuring  $3/4$  in. x  $3/4$  in. to 1- $1/2$  in.. Anode to cathode distances were maintained at  $3/4$  in.. The temperature of the electrolytes was maintained with electric hot plates combined with magnetic stirrers. Water was added to the baths periodically to compensate for evaporation.

#### E. ANALYSIS OF DEPOSITS

For analysis, the alloy deposits were dissolved by treatment with  $6N H_2SO_4$  and a small amount of 30%  $H_2O_2$ . The iron group metals were separated from rhenium by precipitation with hot 5% sodium hydroxide solution. The metal hydroxides (iron group) were then dissolved in  $6NH_2SO_4$  and the metal determined electrolytically from a strongly ammoniacal solution. Rhenium was determined gravimetrically as nitron perrhenate. With alloy deposits weighing approximately 0.2 - 0.3 gms,

the total of the iron group metal and rhenium found in the deposit was consistently above 98% and in some cases above 99%.

#### F. HEAT TREATMENT

The effects of heat treatment on the alloy deposits were determined for temperatures ranging from 316 - 982°C (600 - 1800°F) using 3 specimens from each kind of experiment for each temperature. While most specimens were heated while attached to their substrates, some deposits were detached and then heated. Specimens were placed in an alumina tube and brought up to temperature and held for 1 hour and cooled to room temperature with dry argon or hydrogen atmosphere maintained at a pressure slightly above atmospheric with a flow rate of 500 ml/min.

#### G. HARDNESS MEASUREMENTS

Hardness measurements were made on the cross-sections of the deposits with a Wilson Tukon microhardness tester using a 50-100 gm load and are reported on the Knoop scale. Hardness data plots are presented with a 90% confidence limit which is based on the student "t" distribution for small samplings.

#### H. PHOTOMICROGRAPHS

Cross-sections of specimens were mounted with and without their substrates and polished using diamond abrasives. The polished specimens were etched with a solution of 60 parts lactic acid, 30 parts  $\text{HNO}_3$  + 5 parts HF, by swabbing from 10-15 seconds. The photomicrographs were made with a Polaroid camera using a Leitz MM5 Research Metallograph.

## I. X-RAY ANALYSIS

The diffraction patterns were obtained using the powder Debye Scherrer method. Unfiltered cobalt radiation was employed for an exposure time of 3 hours. The "d" spacings were obtained using the Bragg relation;

$$n \lambda = 2d \sin \theta$$

Lines which represent the "d" spacings of the cobalt-rhenium alloy plating were indexed and conformed to the positions of a Hull-Davey chart<sup>53</sup> for a hexagonal close-packed structure with a c/a ratio of 1.62.

## J. MICRO PROBE ANALYSIS

Alloy coatings were also analyzed with the scanning electron microprobe (Materials Analysis Corp. Model 4005) using a specimen current of approximately 10-20 nano-amps and 25 Kv. The specimens were scanned along the two directions of the mounted cross-sections (i.e., from the substrate to the top layer of the deposit and along the center of the coating parallel to the substrate).

## PART VI

## EXPERIMENTAL RESULTS

## A. EVALUATION OF ELECTROLYTES

The plating baths were evaluated for ease of operation and control of variables in achieving sound and thick alloy deposits. The majority of alloy deposits produced in this study contained concentrations of rhenium ranging from approximately 2-45 weight %, however some deposits were as rich as 75 weight % Re in cases where the rhenium concentrations in the bath were increased accordingly. Some pure rhenium deposits (less than 1 mil in thickness) were produced as standards for surface, micro-probe, and X-ray examinations.

## 1. CONTROL OF PLATING CONDITIONS

The plating conditions employed were the same as those reported in the literature and are included in Table II. Temperature was difficult to control in the earlier experiments at higher operating temperature and generally increased (as high as 5°F) with increasing current density. The pH changes of some of the baths were significant during the longer plating runs .consistently increased or decreased depending on the type bath. When the volume of the electrolyte was increased from 250. to 500 ml better control of the process parameters was realized. In spite of the variations in temperature and pH which slightly altered the cathode current efficiency and % Re deposited, the bath parameters were still within the range in which satisfactory and sound deposits were reported by the referenced investigators.

TABLE II. OPERATING CONDITIONS FOR CODEPOSITING RHENIUM WITH THE IRON GROUP METALS

Bath No.	Alloy	pH	Temp. (°C)	Current Density (Amps/dm <sup>2</sup> )	Anodes	Cathodes	Ref.
1	Ni-Re	4.6	70	1-10	Pt or Ni	Cu	(21)
2	Ni-Re	2.3	70	1.5	Pt or Ni	Cu	(21)
3	Ni-Re	7.6	70	2-12	Ni	Cu or Stainless St.	(21)
4	Ni-Re	4.0	55	2-10	Ni	Cu or Stainless St.	present paper
5	Ni-Re	2.5	70	2	Pt or Ni	Cu or Carbon St.	(24)
6	Co-Re	7.6	70	2-12	Co	Cu, Stainless or Carbon St.	(22)
7	Co-Re	4.0	55	2-10	Co	Cu, Stainless or Carbon St.	present paper
8	Fe-Re	7.6	70	5	Fe	Cu, Stainless or Carbon St.	(22)



The results compiled from the numerous preliminary experiments employing the various baths are presented in Table III.

In general, the performance of the sulfamate bath in the preparation of rhenium alloys was found to be quite satisfactory for the studies which were conducted. The important observation made during the preliminary investigations was that alloy deposits prepared in the sulfamate bath without wetting agent were far less brittle compared to those from electrolytes with wetting agent. It is suspected that the molecules of the wetting agent and the Re ions are depositing at the same time onto the cathode surface which results in structural characteristics different than the role played by wetting agents with pure metals. The sulfamate data in Table III only represents specimens prepared with wetting agent. The only significant difference which appears to be visually evident between these specimens and those prepared without wetting agent, is the presence of fine hairline crack which appear when flexing specimens prepared with wetting agent.

## 2. SURFACE APPEARANCE OF ALLOY DEPOSITS

Table III shows that in the case of the Ni-Re system, thick deposits (4-5 mils) were generally rough when current densities were high. When thick Ni-Re deposits were generally smooth, they were found low in Re content. In the case of the Co-Re and Fe-Re systems, sound, thick and smooth deposits of varying concentrations of rhenium were obtained with an increasing silvery color as the rhenium content in the deposit increased. The surface view of a typical Co-Re

TABLE III. RESULTS FROM PRELIMINARY STUDIES OF THE VARIOUS BATHS

Specimen No.	Bath No.	Alloy	Metal % Re In Bath	C.D. (Amps/dm <sup>2</sup> )	Time	Avg. Thickness (Mils)	pH Change f—f	Wt. % Re		Rate of Deposition Mils/Hr	Visual Appearance of Deposit
								Expected	Analysis		
1	1	Ni-Re	1	1	1 hr	0.3	4.6-4.7	16	15	0.3	smooth with slightly bright silver color
2	1	Ni-Re	1	10	6 min	0.4	4.6-4.8	3.1	No data	4.0	less smooth and dull nickel color
3	2	Ni-Re	1	1.5	2 hrs	1.5	2.3-2.7	70	No data	0.75	dull smooth & discontinuous, dark in spots
4	3	Ni-Re	17	3	2 hrs	0.63	7.6-7.9	40	38	0.32	smooth bright silvery color
5	3	Ni-Re	17	6	2 hrs	2	7.6-8.2	25	26.7	1.0	very smooth & bright & silvery in color
6	3	Ni-Re	17	12	2 hrs	4-6	7.6-7.1	20	16	2.5 avg.	rough & brittle; nickel in color; some darkening
7	4	Ni-Re	0.84	10	1 hr	5	4.0-4.5	-	2	5	semi-smooth nickel color
8	4	Ni-Re	0.84	2	5 hrs	5	4.0-5.1	-	17	1	sandpaper finish with brownish dark gray
9	5	Ni-Re	70	2	3 hrs	3-4.5	2.55-2.35	-	59.6	1.2	very rough but continuous
10	6	Co-Re	17	2	7 hrs	6.5	7.6-7.0	68	25.33	0.93	smooth satin finish - silvery in color
11	7	Co-Re	3.3	2	6 hrs	5	4.0-4.9	-	21.65	0.83	smooth satin finish - silvery in color
12	8	Fe-Re	35	5	2.7 hrs	5	7.5-8.35	63	40.6	1.88	smooth & bright silvery in color

deposit is shown in figure 4 to be crack-free in contrast to chromium deposits (inset) which commonly reveals a crack network due to the release of high residual stresses. Fe-Re deposits were also found to be crack-free. This comparison indicates that these deposits could play a major role in high temperature environments where the substrate must be completely protected from corrosive and erosive gases and liquids.

### 3. WEIGHT % RE IN ALLOY DEPOSITS

Unlike the Ni-Re system, concentrations of rhenium in the Co-Re and Fe-Re alloy deposits prepared in this study were significantly less than the data reported by Netherton and Holt<sup>22</sup> for the same process conditions. In view of this difference one may cast doubt on the accuracy of their data due to the following:

The deposits prepared by the latter authors had a maximum thickness of 0.3 mils (7.5 microns) while the Co-Re and Fe-Re deposits in the present study exceeded four mils (100 microns) in thickness. Their reported weights of alloy deposits used for analysis ranged from 0.06 to 0.15 grams whereas the samples for the present study were over 0.2 grams. Therefore differences could be due to error from their<sup>22</sup> small sample weights and/or in our case to variation in bath behavior when producing thick deposits which are more likely to cause variations in bath compositions.

With the alloy deposits of Co-Re and Fe-Re weighing over 0.2 gms in our present study, the total of rhenium plus cobalt or iron found by wet analysis, ranged from 97.80 - 99.17 weight %. Heating

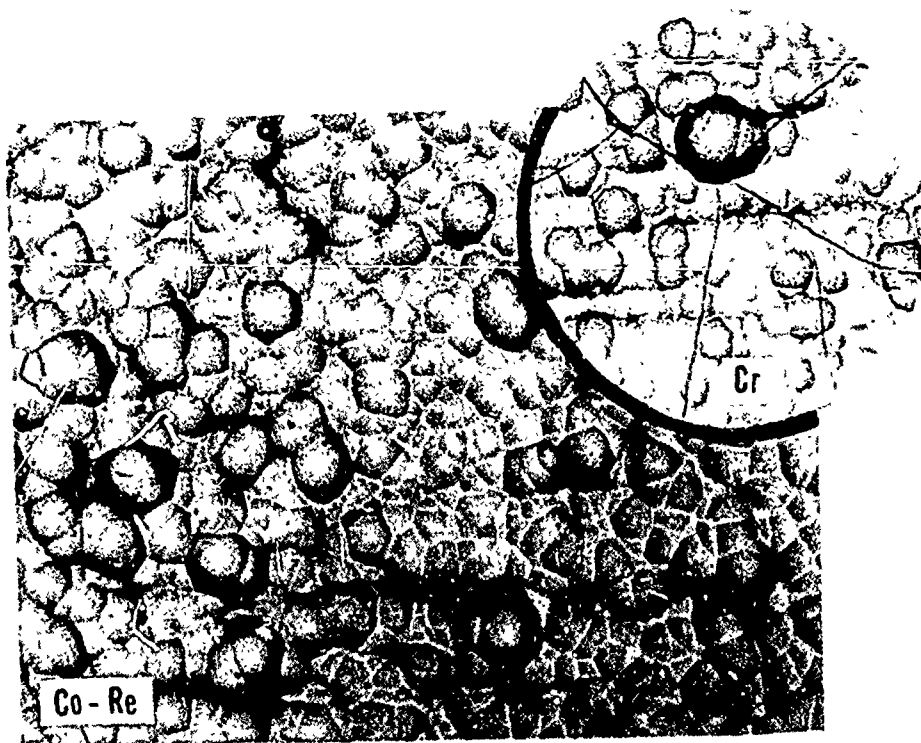


Figure 4. Surface View of Crack-Free Electrodeposited Co-Re in Contrast to Chromium Revealing Stress Cracks... (Original Magnification x200)

the alloy deposits in hydrogen resulted in a weight reduction indicating that oxides or other impurities previously existed. Therefore wet analysis of alloy deposits after heat treat should increase the latter total metal content. Percent values of Re in the Ni-Re deposits for this study were close to those reported by Netherton and Holt<sup>21</sup>. However, it may be worthy to mention that thicknesses were somewhat less (1-2 mils) and sample weights, in this case, were less than 0.2 grams.

The relation of weight percent Re in deposits produced in our studies to that of Re concentration in the bath for the Co-Re systems is given in figure 5. The relation of weight percent Re in the deposit to cathode current density is given in figure 6 for two concentrations of rhenium in the bath for the Co-Re system and one concentration of rhenium for the Ni-Re system.

Reproduced from  
best available copy.



The results show that the Re concentration in the bath has a greater effect on the weight percent Re in the Co-Re deposits than the effect shown by the current density. When the Re content in the bath decreases, the effect of current density on deposit composition of the Co-Re system increases. In the case of the Ni-Re system a sharp initial drop in Re concentration occurs when first increasing the current density.

#### 4. MICROSTRUCTURES OF RHENIUM ALLOYED WITH IRON GROUP METALS

The crystal structure of electrodeposited alloys can best be obtained by X-ray analysis which will be discussed later. However, the microscopic examination of the cross-section of deposits is also of considerable interest as it reveals the microstructure or growth

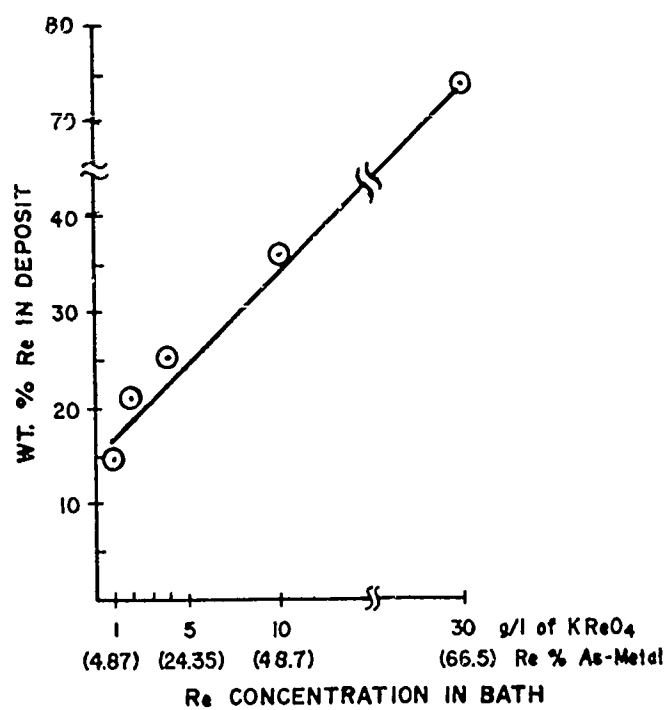


Figure 5. Relation of Deposit Composition with Bath Concentration with Respect to Rhenium in Co-Re Electrodeposits (Bath 6)

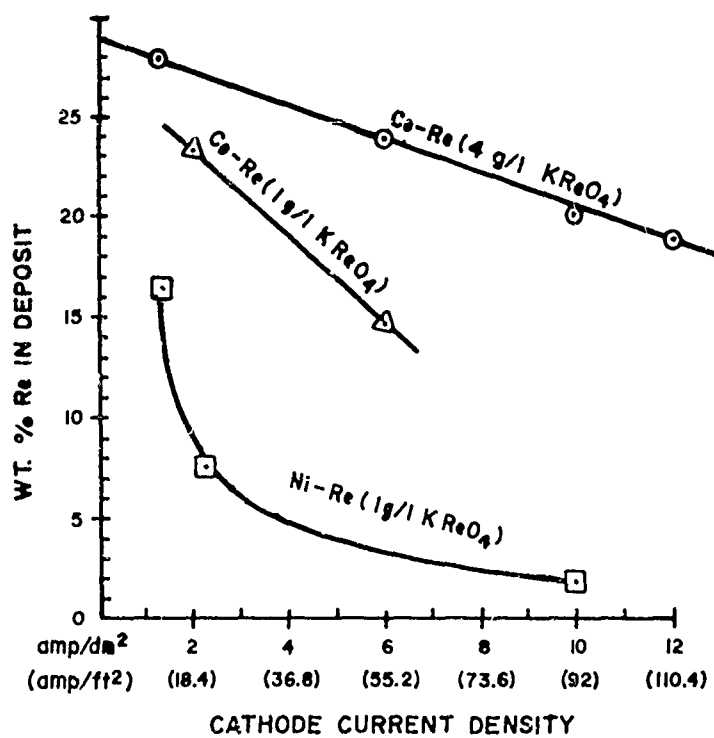


Figure 6. Relation of Deposit Composition with Cathode Current Density Using Bath 3 and 6

habit characteristics of electrocrystallized alloys. Since it is beyond the resolution of the ordinary microscope to single out actual grains, Brenner<sup>54</sup> has suggested that possibly the term texture would be more appropriate since an aggregation of grains or crystals is probably observed in the microstructures of electrodeposited alloys.

Electrodeposited alloys are in many respects similar to those of the individually deposited metals in that the grain size is smaller than that of thermal alloys<sup>54</sup>. The microstructure of alloys studied in the present investigation exhibited either fibrous columnar structure or a laminar structure and in many cases exhibit both structures combined. The latter microstructures are somewhat similar to those reported for other alloy systems<sup>54,55</sup>. The photomicrographs in figures 7 through 9 represent microstructures of some of the alloy specimens listed in Table III. The microstructures representing the Ni-Re system appear to be significantly affected by factors such as the type bath, current density and rhenium concentration in the deposit. Unlike Ni-Re, the microstructure of Co-Re and Fe-Re deposits appear quite similar regardless of the bath or plating conditions employed (figure 9).

##### 5. OBSERVATIONS OF SOME GROWTH HABITS

The formation of preferential sites for electrocrystallization is strongly influenced by impurities and high metal ion concentration gradients on the cathode surface which may result in nodular and heterogeneous growth. One type of an erratic growth change from laminar to tree-like or dendritic texture is shown in figure 7e for



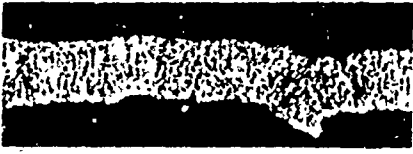

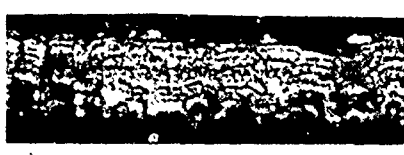
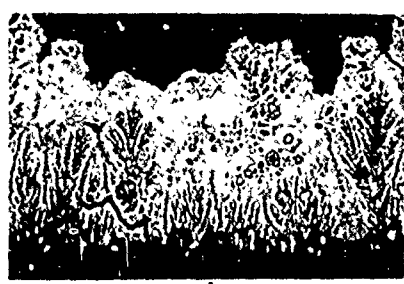

BATH NO.	Ni-Re ALLOYS	CURRENT DENSITY (amp/dm <sup>2</sup> )	% Re IN BATH AS-METAL	DEPOSIT THICKNESS (MILS)	DEPOSIT COMP (WT. % Re)
1	 a x1000	1	1	0.35	15
1	 b x1000	10	1	0.40	3
3	 c x1000	3	17	0.63	48
3	 d x500	6	17	2.5	—
3	 e x500	12	17	5	—

Figure 7. Microstructures and Properties of Ni-Re Alloys Electrodeposited Under Various Plating Conditions (Cross-Sectioned Perpendicular to Base Metal)

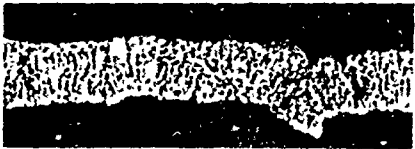


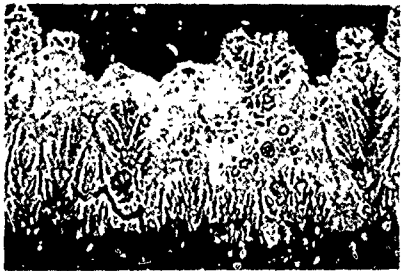

BATH NO.	Ni-Re ALLOYS	CURRENT DENSITY (amp/dm <sup>2</sup> )	% Re IN BATH AS-METAL	DEPOSIT THICKNESS (MILS)	DEPOSIT COMP (WT. % Re)
1	 a X1000	1	1	0.35	15
1	 b X1000	10	1	0.40	3
3	 c X1000	3	17	0.63	48
3	 d X500	6	17	2.5	—
3	 e X500	12	17	5	—

Figure 7. Microstructures and Properties of Ni-Re Alloys Electrodeposited Under Various Plating Conditions (Cross-Sectioned Perpendicular to Base Metal)


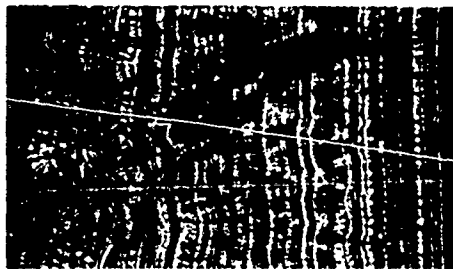

BATH NUMBER	4	4	5
THICKNESS (Mils.)	<div><div>5 4 3 2 1 0</div><div></div></div>	<div></div>	<div></div>
% Re IN BATH AS-METAL	.84	.84	70
CURRENT DENSITY amp/dm <sup>2</sup>	2	10	2
DEPOSIT COMPOSITION WT. % Re	approx. 20	2	59.6
HARDNESS (Knoop)	—	525	725

Figure 8. Microstructures and Properties of Ni-Re Alloys Electrodeposited Under Various Plating Conditions (Cross-Sectioned Perpendicular to Base Metal)

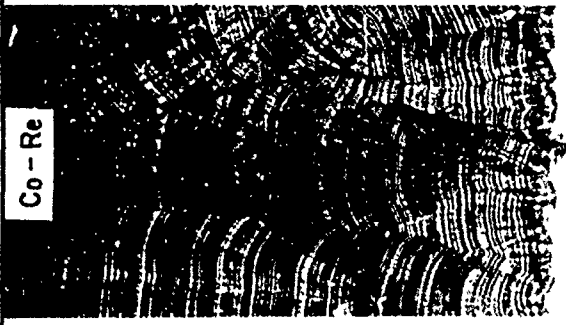
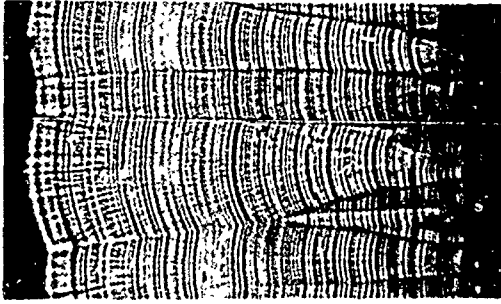

BATH NUMBER	6	7	8
THICKNESS (Mils.)	 (a) X500	 (b) X500	 (c) X500
% Re IN BATH AS-METAL	19.46	3.3	35
CURRENT DENSITY amp/dm <sup>2</sup>	2	2	5
DEPOSIT COMPOSITION WT. % Re	25.33	21.65	40.6
HARDNESS (Knoop)	550	610	529

Figure 9. Microstructures and Properties of Co-Re and Fe-Re Alloys Electrodeposited Under Various Plating Conditions (Cross-Sectioned Perpendicular to Base Metal)

the Ni-Re system, possibly due to diminishing Re ions. Figure 10a and 10b show formation of cones or columnar growth habits similar to pure cobalt which were found to have higher concentrations of cobalt compared to the unetched matrix when examined by the microprobe.

It is speculated that the formation of these cones is triggered by clinging hydrogen bubbles or impurities which settle on the cathode surface during electrodeposition and initiate a condition for the rate of growth to predominate over the rate of nucleation. The shielding by clinging gas bubbles or non-metallic impurities would increase the cathode current density around the minute shield which results in less deposition of rhenium. Another observation from the review of Co-Re microstructures is the occasional appearance of stress cracks which initiate at the interface rather than the surface which appears to occur occasionally only with high rhenium concentrations in the deposit when deposited on steel. (See figure 10c).

#### 6. EVALUATION OF PLATING BATHS AND ALLOY SYSTEMS

PLATING BATHS - From the standpoint of plating baths for producing rhenium alloys, a choice cannot justly be made without experimentation. For example it was shown that while the sulfamate bath did not produce satisfactory Ni-Re deposits with high Re contents, the same sulfamate bath formulation with cobalt in place of the nickel ions produced satisfactory deposits. Therefore the alloy system, rather than the bath appears to be the problem. It is believed that bath 6 and 7 and possibly even bath 5 (with Co in place of Ni) would

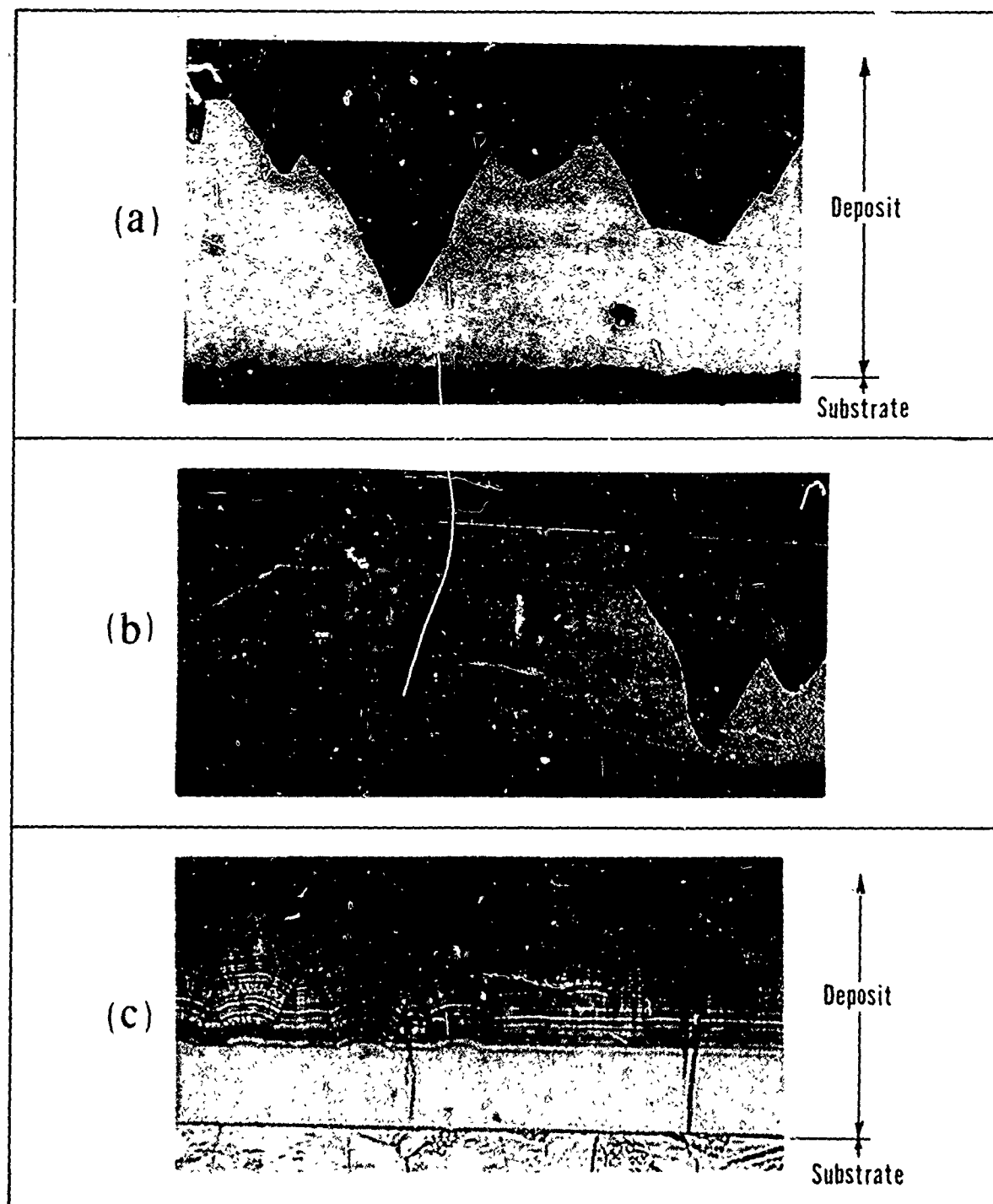


Figure 10. Some Growth Habits of Cross Sectioned Co-Re Electrodeposited Alloys From Bath 6 ..... (Original Magnification x500)

be satisfactory for producing Co-Re deposits. However, extended studies would be necessary to determine the advantages of one bath over the other.

ALLOY SYSTEMS - Based on the data compiled up to this point of the study, the Co-Re and Fe-Re alloy systems appear most promising. The reproducibility of results in obtaining sound, smooth and thick deposits of Co-Re alloys has been demonstrated sufficiently to justify more concentrated studies with this alloy system.

Due to a change in deposition conditions, various phases of the phase diagram of a particular alloy system can appear in a coating while the mean composition of an alloy electrodeposit does not change. Therefore, the selection of an alloy with a wide range of solubility to form a continuous series of solid solutions should be most preferable. This makes the Co-Re system the best candidate since a change in composition should produce no compounds or additional phases and from the standpoint of problems inherent in electrolysis, deposits of Co-Re were much more satisfactory than Ni-Re.

#### B. EVALUATION OF Co-Re ALLOYS

The extended studies with the Co-Re system were conducted with the use of baths 6 and 7. The results of the studies are presented as follows:

##### 1. RELATION OF HARDNESS TO HEAT TREATMENT OF Co-Re ALLOYS

The most significant characteristic of Co-Re deposits after heating is the significant increase in hardness which generally approaches a maximum somewhere between 600-1200°F. This effect is

shown in figure 11 for two Co-Re alloys which were prepared with the citric bath number 6 and compared with pure cobalt produced in the same basic electrolyte and plating conditions. This behavior of increased hardness is reported to be characteristic of other alloy deposits according to Brenner<sup>56</sup>. He attributes this increase to precipitation hardening which is convincing with the cobalt-tungsten system since it is a precipitation hardenable alloy. However, one can not be as easily convinced when studying alloy systems in which no precipitates are known to form. Some evidence for explaining the increase of hardness after heating Co-Re alloys may be found in the X-ray data which will be discussed later.

Brenner also reported that the maximum hardening which occurs with the electrodeposited alloys previously studied was obtained within a narrow range of temperature which depends on the type of alloy<sup>56</sup>. However the maximum hardness exhibited by the Co-Re alloys covers a broader range of temperature (see later plots).

## 2. EFFECT OF HEAT TREATMENT ON MICROSTRUCTURE OF COBALT AND COBALT RHENIUM ALLOY

The changes in microstructure of the pure cobalt and Co-Re (27%) deposits corresponding to the hardness plot in figure 11 are presented in figure 12. The photomicrographs clearly show the recrystallization and annealing which took place with pure cobalt while the alloy still appears to be recrystallizing at the highest temperature with the laminar structure slowly disappearing. The latter changes in microstructure appear to be in line with the microhardness changes shown in figure 11.



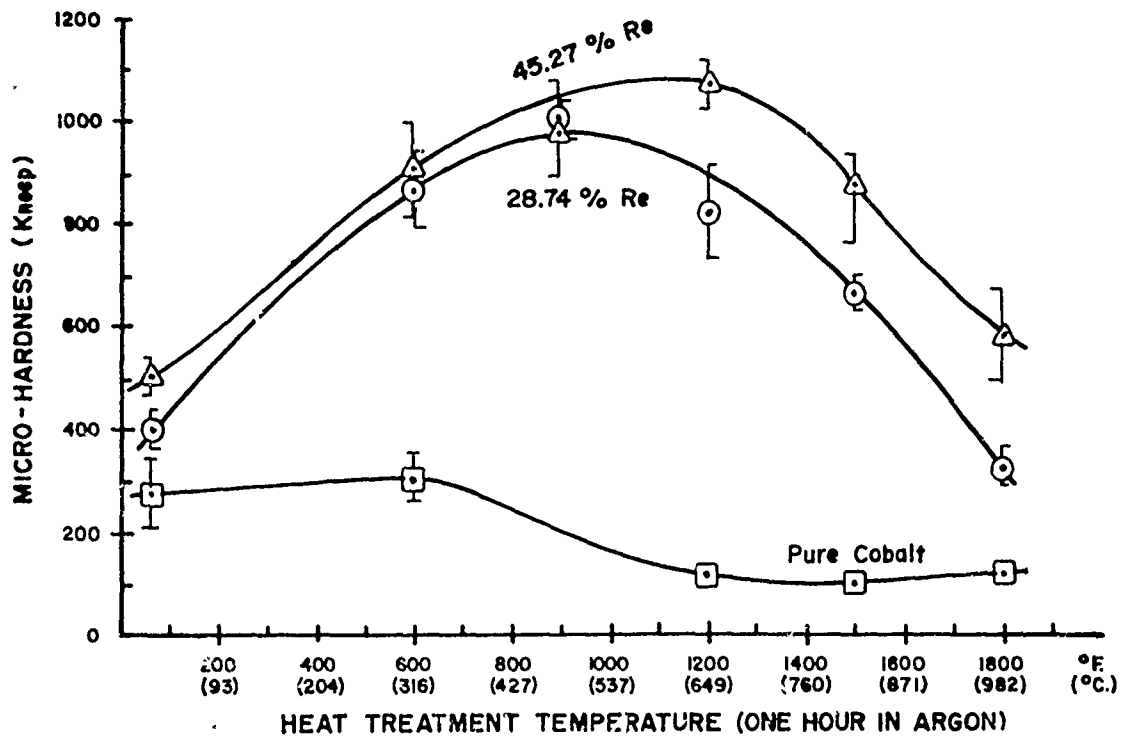


Figure 11. Relation of Room Temperature Microhardness to Heat Treatment of Electrodeposited Cobalt and Cobalt-Rhenium Alloys. (Bath 6)


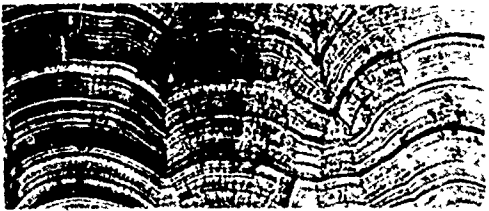
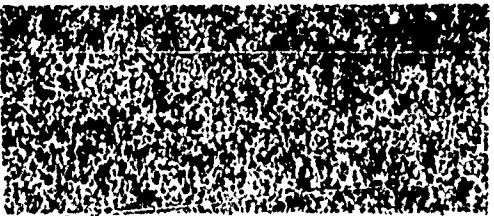

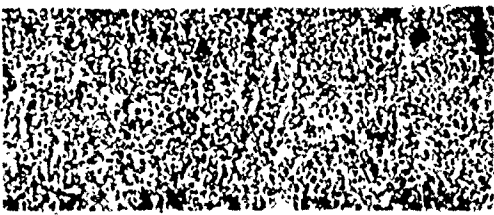


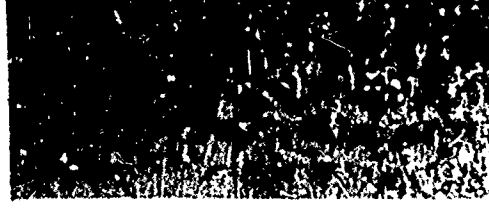
HEAT TREAT (°F)	COBALT	COBALT-RHENIUM (28.74 WT.%)
AS-PLATED		
1200		
1500		
1800		

Figure 12. Effect of Heat Treatment (in Hydrogen Atmosphere) on the cross Sectional Microstructures of Electrodeposited Cobalt and Cobalt-Rhenium Alloy (28.74 wt. % Re) From Bath 6.....Original Magnification X500)

### 3. EFFECT OF Re-CONCENTRATION ON HARDNESS

It was previously mentioned that the properties of metals and alloys prepared by electrodeposition can be significantly altered by the plating conditions in contrast to those thermally prepared. For example, a large range of hardness values can be obtained with as-plated deposits by merely changing the bath temperature, pH or the current density in addition to impurities in the deposit. Therefore it is difficult to obtain the relation of Re content with hardness in as-plated deposits, since its effect is superimposed with other effects. However, the examination of hardness values of a group of specimens after being subjected to heat treatment at various temperatures has revealed that a relationship is first detected after annealing the deposits for one hour at 1200°F. The relation of hardness vs. Re content in the deposit is shown in figure 13 for the 1200°F and 1800°F treatments.

A comparison is also made between specimens heated in an argon atmosphere and those in a hydrogen atmosphere. Heat treatment of Co-Re deposits in a hydrogen atmosphere consistently exhibited higher hardness values than those heated in argon. Evidence from this study to explain the cause of hardness difference due to atmospheres is not possible.

### 4. HARDNESS BAND OF Co-Re ALLOYS

Since plating effects are superimposed with alloying effects in altering the hardness of alloy deposits, it was decided to plot a hardness band which represented all of the specimens which fall into

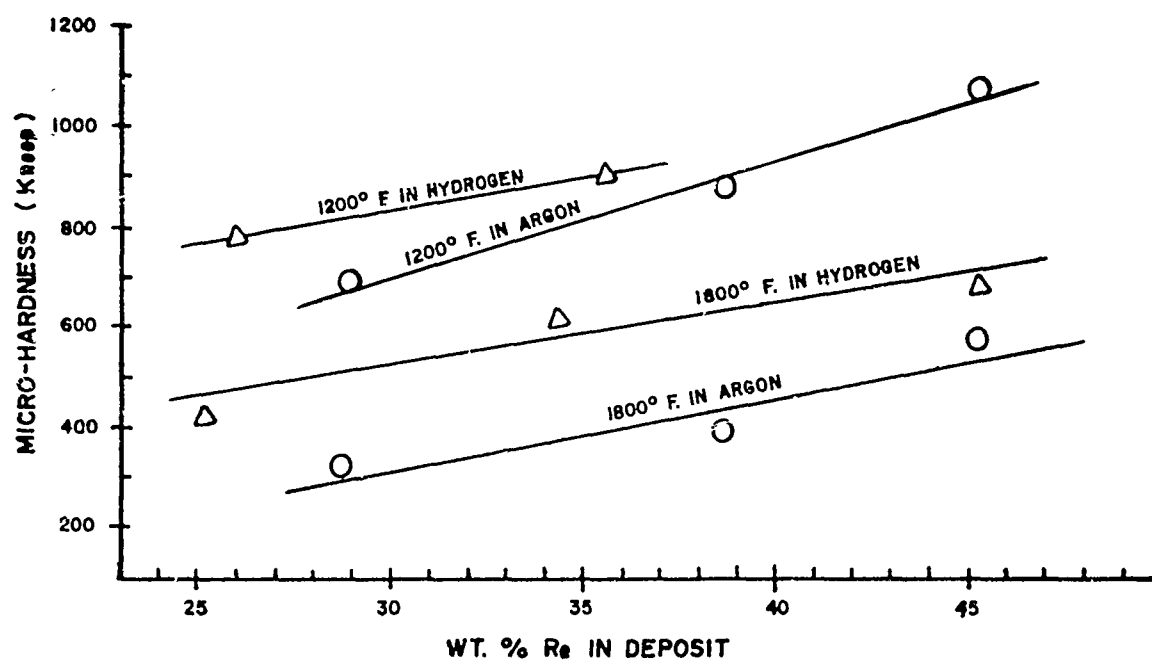


Figure 13. Relation of Room Temperature Microhardness to Wt % Re in Cobalt Alloy Deposits for Two Heat Treatments and Two Atmospheres. (Combined Data From Baths 6 and 7)

the composition range of 15-45 weight percent (figure 14). The hardness of these alloys appeared to increase rapidly with the first additions of Re which then decreased in rate with higher additions. However, the cause could not always be attributed to the Re alone. Alloy deposits with Re contents exceeding approximately 45 weight percent were generally found to be too brittle and exhibited numerous cracks during metallographic polishing. As a safe estimate, Co-Re and Fe-Re alloys exceeding 45 weight percent Re are not recommended for thick deposits until improved process conditions can be established. Alloys below 15 weight percent Re are not cracked but have not been presented in the hardness band due to insufficient data.

A sound reason for the increase in hardness of Co-Re after heat treatment cannot be offered at this point of the study. However, the X-ray data may provide some strong evidence for the behavior.

The photomicrographs shown in figure 15 represent the general microstructures observed before and after heating Co-Re alloys with the respective concentrations of Re ions in the bath and presumably corresponding increase of Re in the deposit. As the Re increases in the as-plated deposits, the laminar interfaces generally become finer. Some cracks can be observed after heating the deposit prepared in the 30 g/l bath. An interesting observation is the refinement of the as-plated laminae and resultant structure after heating of the deposit, which contains the dispersed sub-micron  $Al_2O_3$  particles.

## 5. RELATION OF HARDNESS TO HEAT TREATMENT OF DISPERSION

### HARDENED Co-Re ALLOYS

One group of Co-Re specimens were prepared by dispersing sub-micron ( $.05\mu$ )  $Al_2O_3$  particles in the matrix alloy during

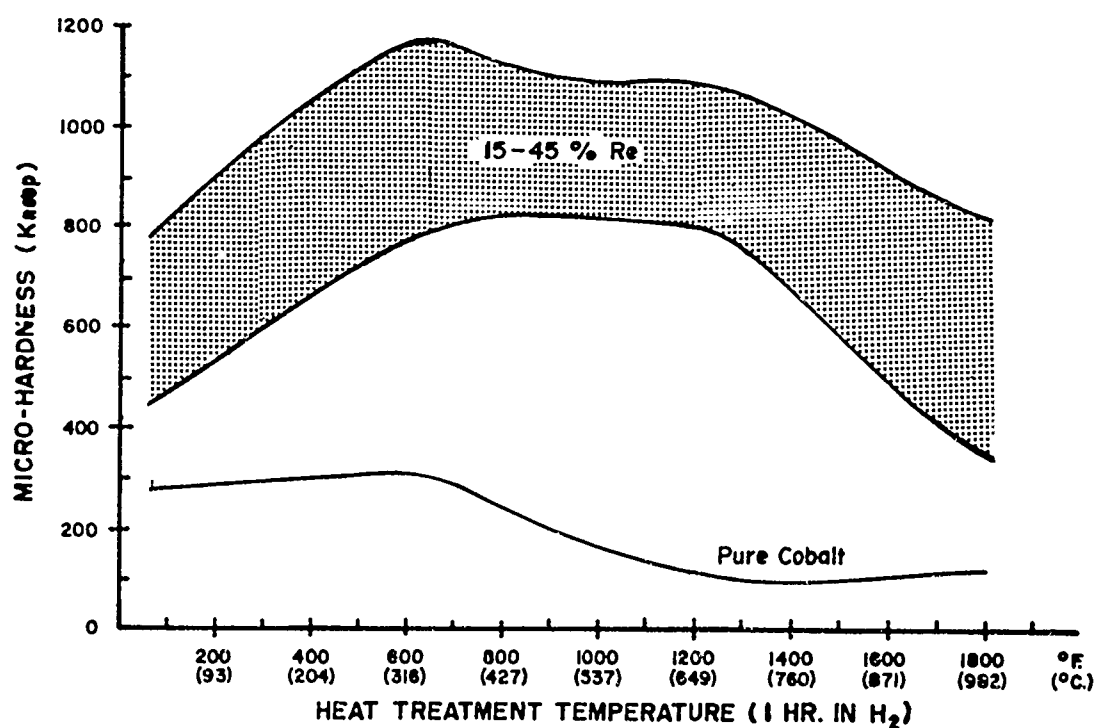


Figure 14. Microhardness Band of Co-Re Alloys vs Heat Treatment (Combined Data From Baths 6 and 7)






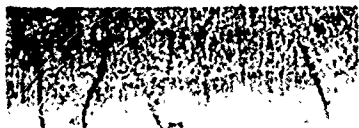


BATH CONTENT (KReO <sub>4</sub> )	AS-PLATED	AFTER HEAT TREAT (1800° F)
4 g/l		
10 g/l		
30 g/l		
4 g/l (PLUS 50 g/l Al <sub>2</sub> O <sub>3</sub> )		

Figure 15. Microstructures of Various Cross Sectioned Co-Re Alloys (Bath 6) before and After Heat Treatment at 1800°F....(Original Magnification: X500)

electrodeposition. Solution strengthening and dispersion strengthening were combined to determine the effects of the particles on the properties of the Co-Re alloys. The change of hardness after heat treatment for one of the alloys is presented in figure 16. The results show that the particles significantly increase the hardness of the Co-Re alloy throughout the heat treatment temperature range as compared to the general profile of Co-Re alloys without particles (see figure 11) and subsequently retards the recrystallization and softening of the alloys during heating. It should be mentioned that these sub-micron size particles do not cause the degradation effects as the previously mentioned gross foreign particles which decompose upon heating.

The data presented in figure 16 again demonstrates the effect of heat treat atmosphere on hardness with hydrogen producing the harder deposits even with dispersion hardened alloys.

The photomicrographs of Co-Re with dispersed  $Al_2O_3$  shown in figure 15 are representative of the microstructure for the given alloy for the as-plated and heat treated (1800°F) condition.

#### 6. X-RAY EXAMINATION OF COBALT-RHENIUM ALLOYS

The X-ray data showed that the as-plated specimens were alloys of Co-Re of variable composition. However the specimens did not all consist of single phase alloys of Co-Re as one might expect from reviewing the equilibrium diagram. Instead, in some cases both the HCP and cubic phase were detected in as-plated and also heat treated specimens. It was also shown that heat treatment promoted the formation of oxides of cobalt in the majority of specimens. The X-ray



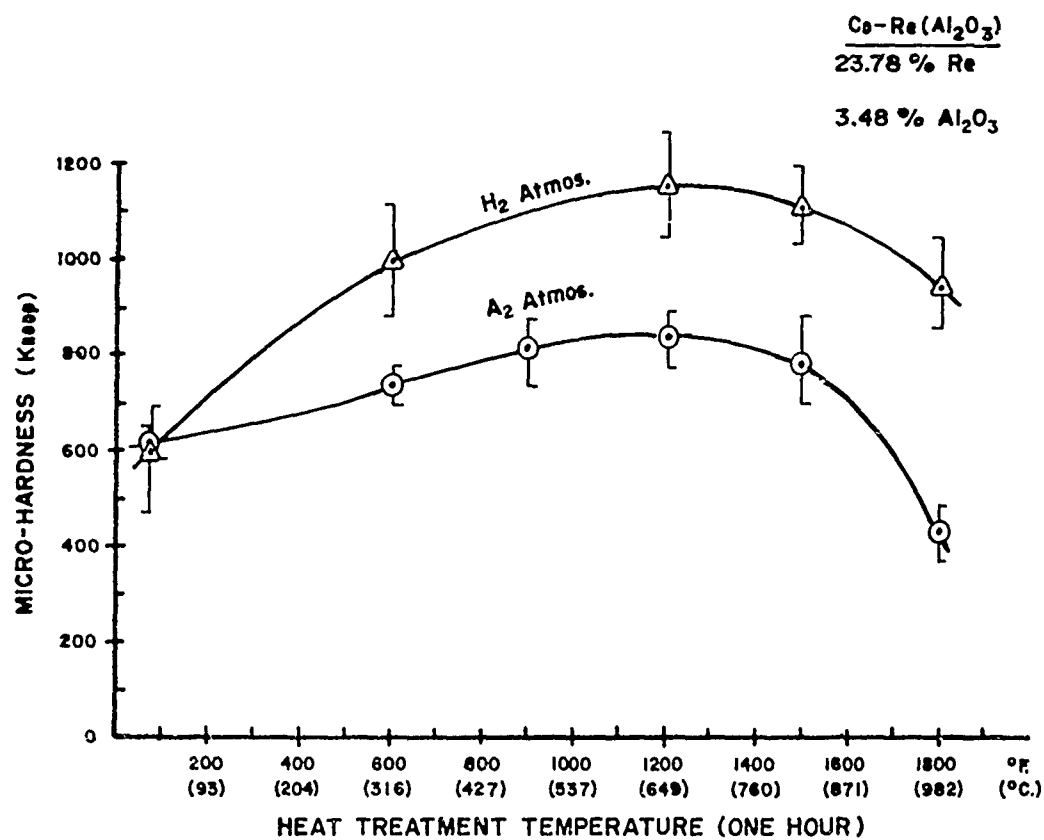


Figure 16. Relation of Room Temperature Microhardness to Heat Treatment for a Co-Re ( $\text{Al}_2\text{O}_3$ ) Alloy (Bath 6)

data from 4 specimens (prepared in Bath No. 6) subjected to various temperatures of heat treatment are given in table IV. The change from broad to sharp lines of the diffraction profiles after heating corresponds somewhat with the microstructural changes from fine to coarse grains observed under the microscope. The phases detected indicates the existence of two behaviors:

a. Specimens 96 and 97 which have 20 - 25 wt % Re contain a Co-Re phase with a cubic structure. When the Re % is increased or when  $Al_2O_3$  is present as with specimen 50 and 52, no cubic structure is found. The Co-Re alloys with both the HCP and cubic phases existing indicates that the alloy is not in equilibrium.

Koster and Horn<sup>57</sup> have presented data (see inset in figure 2) which shows the maximum point of  $\alpha$ -Co (cubic) in the equilibrium diagram to exist at 25 atomic % Re (which is above 50 wt % Re) at 1500°C rather than 15 wt % Re as it is shown by Savitskii and Tylkina. The X-ray data in table IV seems more consistent with the phase diagram presented by Koster and Horn. One can conclude from the table that when plating alloys having 20 - 25 wt % Re such as Specimen No. 96,  $\alpha + \beta$  phases may exist in the as-plated condition and the two phases may still persist after heat treatment indicating a non-equilibrium condition. This condition is similar to what one would expect if the Co-Re alloy was heated up to the  $\alpha + \beta$  zone of the phase diagram and then cooled by quenching whereby the cubic phase ( $\alpha$ ) is retained in a matrix of Co-Re (HCP) which is represented as the  $\beta$  phase.

TABLE IV. X-RAY DATA OF VARIOUS Co-Re ALLOYS

Specimen No.	Heat Treat	PHASES AND STRUCTURES DETECTED			DIFFRACTION PROFILES	CONDITION
		Co-Re(HCP)	Co-Re(Cubic)	Oxides		
96 (approx. 20-25 wt. % Re)	as-plated	Predominant	Some	None	broad lines	Small grain size; highly strained structure
	800°F	Predominant	None	None	less broad	TRANSITION
	1200°F	Predominant	Some	Trace of CoO	broad to sharp	Recrystallizing; increasing grain size; decreasing defect structure.
	1800°F	Predominant	Some	Trace of CoO	increased sharpness	
97 (approx. 20-25 wt. % Re)	as-plated	NOT RECORDED			broad lines	Relatively small grain size; highly strained structure
	800°F	Predominant	None	Trace of CoO	broad to sharp	TRANSITION
	1200°F	Predominant	None	Trace of CoO	increased sharpness	Recrystallizing; increasing grain size; decreasing defect structure.
	1800°F	Less Predominant	Some	Increasing CoO		
50 (45 wt. % Re)	as-plated	Predominant	None	None	broad lines	Small grain size; highly strained structure
	800°F	Predominant	None	None	less broad	TRANSITION
	1200°F	Predominant	None	None	broad to sharp	
	1500°F	Predominant	None	Increasing amt. of CoO and Co <sub>3</sub> O <sub>4</sub>	increased sharpness	
	1800°F	Predominant	None	Trace of CoO	sharp	Recrystallizing; increasing grain size; decreasing defect structure
52 (24 wt. % Re) 3.5 wt. % Al-0.3	as-plated	Predominant	None	None	broad lines	Small grain size; highly strained structure
	800°F	NOT RECORDED			broad to sharp	TRANSITION
	1200°F	Predominant	None	Some CoO	increased sharpness	
	1500°F	Predominant	None	Some CoO	sharp	
	1800°F	Predominant	None	Increasing amt. of CoO and Co <sub>3</sub> O <sub>4</sub>		Recrystallizing; increasing grain size; decreasing defect structure

b. Varying amounts of oxides of cobalt were detected in the majority of specimens after subjecting them to the various temperatures of heat treatment as indicated in table IV. Since oxygen was not introduced during heat treatment, it must be assumed that oxygen must have been present in the matrix of the as-plated deposits. (In order to minimize the formation of oxides, specimens probably should be heat treated in a vacuum furnace.)

The existence of the oxides, formed upon heating the specimens, may be a contributing factor in the increase in hardness occurring after heat treatment. However, the extent of oxide formation detected, after heating the specimens at the different temperatures, does not correspond exactly with the hardness measurements for the same temperatures.

## PART VII

### CONCLUSIONS

The data compiled in the present investigation offers the following conclusions.

1. Smooth, sound, thick and crack free alloy deposits of Co-Re and Fe-Re (up to approximately 60 weight percent Re) can be successfully produced. While sound and crack-free Ni-Re deposits can be successfully produced, thick deposits with the higher concentrations of Re (i.e. approximately 16 wt. % Re) require more development work.

2. Post heat treatment of Co-Re alloys significantly increase their hardness at the 600°F heat treatment temperature level and the hardness decrease does not generally occur until after a 1500-1800°F heat treatment cycle. The hardness drop is generally smaller as the amount of Re is increased, and in only a few cases does the hardness fall below the as-plated value.

3. The microstructures of Co-Re and Fe-Re alloys are laminar superimposed over the columnar type structure. The columnar structure is typical for the electrodeposited single iron group metals.

4. Based on the microstructures and hardness changes, recrystallization for pure cobalt appears to be complete at approximately 1200°F above which annealing takes place. In the case of Co-Re alloys, laminations do not completely disappear until heated at approximately 1800°F at which recrystallization is still taking place with the degree of recrystallization being generally lesser with increase in Re content.

5. Dispersion strengthening of Co-Re alloys was very effective in refining the microstructure and their hardness profile for the various heat treatments.

6. Continuous filtration of the electrolyte during plating is recommended to prevent gross foreign particles from entering the matrix of the deposit which decompose upon heating and subsequently produce structural defects in the deposit.

7. The heating of Co-Re specimens in a high vacuum and at a longer time should significantly increase their qualities by

minimizing oxide formation and approaching the state of equilibrium and homogenization.

PART VIII  
RECOMMENDATIONS

1. Further studies should be conducted to determine which bath is most superior - the sulfamate or the citric bath, from the standpoint of process controls and reproducibility of alloy deposits.
2. Other engineering properties of electrodeposited rhenium alloyed with Co and Fe should be determined.

## PART IX

## LITERATURE CITED

1. Blum, W., Hogaboom, G.B., "Principles of Electroplating and Electroforming" 3rd Ed., McGraw-Hill Book Co. Inc., N.Y. pp. 348-349 (1949).
2. Lowenheim, F.A., "Modern Electroplating" Edited by Gray, A.G., John Wiley and Sons Inc., N.Y. Sec 18, pp. 483-500 (1953).
3. Brenner, A., "Electrodeposition of Alloys" Vol. II Academic Press, N.Y. pp. 347-456 (1963).
4. Raub, E. and Muller, K., "Fundamentals of Metal Deposition" Elsevier Publishing Co., N.Y. p. 136 (1967).
5. Sims, C.T., Craighead, C.M., Jaffee, R.I., Gideon, D.H., Wyler, E.N., Todd, F.C., Rosenbaum, D.M., Sherwood, E.M., and Campbell, I.E., "Investigations of Rhenium", WADC Tech Percrt #54-371, (June 1954).
6. Sims, C.T., Wyler, E.N., Gaines, G.B., Rosenbaum, D.M., "A Survey of the Literature on Rhenium", WADC Tech Report #56-319 (Astia Document No. AD 110596) (June 1956).
7. Sims, C.T., Craighead, C.M., Jaffee, R.I., Gideon, D.H., Kleinschmidt, W.W., Nexsen, Jr. W.E., Gaines, G.B., Todd, F.C., Peet, C.S., Rosenbaum, D.M., Runck, R.J., Campbell, I.E., "Investigations of Rhenium", WADC Tech. Rept. #54-371 Supplement 1 (ASTIA Document No. AD 97301) (Sept. 1956).
8. Gonser, B.W., (Editor) "Rhenium", Elsevier Publishing Co., N.Y. (1962).
9. Port, J.H., "Recent Developments in Rhenium and Rhenium Alloy Technology" Plansee Proceedings p. 613-635, 1964, Benesovsky, F., (Editor) Reutte/Tyrol, Metallwerk Plansee, AG, 1965.
10. Fink, C.G., Deren, P., "Rhenium Plating", Trans. Electrochemical Soc., 66, p. 471 (1934).
11. Fink, C.G., and Deren, P., U.S. Patent 2,138,573 (1938).
12. Young, C.B.F., Metal Ind. (N.Y.), 34, p. 176 (1936).
13. Hetherton, L.E., and Holt, M.L. "Electrodeposition of Rhenium from Aqueous Solutions", Trans. Electrochemical Soc. 95, p. 324 (1949).

14. Levi, R., U.S. Patent 2,616,840 (Nov 4, 1952)
15. Korovin, N.V., and Ronzhin, M.N., "Electrodeposition of Rhenium from Ammonium Sulphate Solutions", Russian Jol. of Phys. Chem. Vol. 35, No. 3, p. 320-322 (March 1961).
16. Kvokova, I.M., and Lainer, V.I., "Electrodeposition of Thick, Dense Rhenium Coating," (UDC 621.357.7) Translated from Zashchita Metallov, Vol. 1, No. 5, p. 518-520, (Jan 1965).
17. Camp, E.K., "Recent Developments in the Application and Electroplating of Rhenium" Plating, Vol. 55, No. 2, p. 413 (May 1965).
18. Camp, E.K., "Tarnishing of Thin Rhenium Deposits on Nickel" "Effect of Plating Process Anions and Ultrasonics", Plating, p. 318 (Mar 1966).
19. Nikitina, A.A., and Sominskaya, Z.M., "The Electrodeposition Mechanisms of Rhenium", Zashchita Metallov, Vol. 2, No. 3, p. 349 (Translated), May-June, 1966.
20. Root, G.S., and Beach, J.G., Ref (8) p. 181-188.
21. Netherton, L.E., Holt, M.H., "Electrodeposition of Rhenium-Nickel Alloys" J. Electrochemical Soc., Vol. 98, p. 106 (Mar 1951).
22. Netherton, L.E., Holt, M.H., "Electrodeposition of Rhenium - Cobalt and Rhenium - Iron Alloys", J. Electrochemical Soc., Vol. 99, p. 44 (Feb 1952).
23. Savitskiy, Y.M., Tytkina, M.A., and Povarova, K.B., "Rhenium Alloys" JPRS 34, 566 (15 Mar 1966) (Translation of book entitled Splavy Rheniya, Moscow, "Nauka" Publishing House), (1965).
24. Korovin, N.V., and Ronzhin, N.M., "Cathodic Deposition of Rhenium Nickel Alloy from Ammonium Perrhenate Electrolyte", translated from Zhurnal Prikladnoi Khimii, Vol. 33, No. 12, pp/ 2734-2738 (April 9, 1960).
25. Sims, C.T., Craighead, C.M., and Jaffee, R.I., "Physical and Mechanical Properties of Rhenium", J. of Metals (Transaction AIME) p. 168-179 (Jan 1955).
26. Ref. (9), p. 616.



27. "Metals Handbook" Vol. 1, 8th ed. ASM Metals Park, Noveltv, Ohio n. 1220 (1961).
28. Ref. (8), p. 61.
29. Ref. (8), n. 163.
30. Ref. (8), n. 27, Ref. (6) n. 110, Ref. (17) n. 413.
31. Ref. (8), p. 175-180.
32. Tamashov, N.D., and Matveev, T.V., "Corrosion and Electrochemical Behavior of Rhenium", Zashchita Metallov, Vol. 2, No. 1, p. 57 (Translated) Jan-Feb 1966.
33. Druce, J.G.F., "Rhenium", Macmillan, New York, 1948.
34. Pauling, L., "Unsolved Problems of Structural Chemistry", Chem. Eng. News, 25 n. 2970, 3045 (1947).
35. Rabinowicz, E. "Friction and Wear Properties of Rhenium", WEAR, 10 p. 313, 318 (1967).
36. DePew, J.R., and Larsen, T.L., "Electrodeposition of Rhenium for Wear Resistance", presented at the 57th National Convention of the Amer. Electroplaters Soc. in Montreal, Canada, Jun 21-25 1970.
37. Buckely, D.H. and Johnson, R.L., "Frictions and Wear of Hexagonal Metals and Alloys as Related to Crystal Structure and Lattice Parameters in Vacuum", ASLE Trans., 9 n. 121-132 (1966).
38. Turns, E.W., (General Dynamics, Ft. Worth, Texas) "Industrial Development of the Silver-Rhenium Alloy Plating Process", presented at the 57th National Convention of the Amer. Electroplaters Soc. in Montreal, Canada, June 21-25, 1970.
39. Ref. (8), p. 181-188.
40. Brenner, A., "Electrodeposition of Alloys", Vol. I, Academic Press, N.Y. 1963.
41. Ref. (2), n. 64.
42. Delahay, P. "New Instrumental Methods in Electrochemistry", Interscience Publishers, Inc. N.Y., p. 28, 1954.

43. Latimer, W.M., "Oxidation Potentials", 2nd ed., Prentice Hall, Englewood Cliffs, N.J., p. 243, 1952.
44. Ref. 40, p. 267-273.
45. Eliot, R.P., 1st Supp., "Studies of Binary Alloys", McGraw Hill Book Co., Inc., p. 667, 1965.
46. Ref. 45, p. 331.
47. Hansen, M., "Studies of Binary Alloys", 2nd ed., McGraw Hill Book Co., Inc. N.Y., p. 495, 1958.
48. Ref. 47, p. 702.
49. Ref. 6, p. 47.
50. Sautter, F.K., J. Electrochem. Soc. 110, 557 (1963).
51. Browning, M.E., Leavenworth Jr., H.W., Webster Jr., W.H. and Dunkerley, F.J., "Deposition Forming Processes for Aerospace Structures", ML-TDR-64-26 (Feb. 1964).
52. Greco, V.P. and Balnauf, W., Plating Journal, pp 250-257, March 1968.
53. Azaroff, L.V. and Buerger, J.W., "The Powder Method in X-ray Crystallography", McGraw-Hill Book Co., N.Y. pp 56-78 (1958).
54. Ref. 40, p. 175-182.
55. Ref. 4, p. 147.
56. Ref. 40 p. 211-215.
57. Koster, W., and Horn, E., "Phase Diagrams and Lattice Constants of the Alloys of Cobalt with Rhenium, Ruthenium, Osmium, Rhodium, and Iridium", Z. Metallkunde, 43, 444-9 (1952).